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JOURNAL

OF

THE CHEMICAL SOCIETY.

University of Toronto

I.—*On Ozone.*

By Charles Daubeny, M.D., F.R.S.

That a substance called ozone, characterised by a peculiar smell and by remarkable oxidising properties, may be generated by artificial means, is a fact upon which I presume all chemists are agreed; and as one of the readiest means of obtaining it is by the passage of electrical sparks through air containing oxygen, it can hardly be doubted, that whenever during a thunder-storm the same odour is perceived, it is owing to the generation of this principle by atmospheric electricity.

Ozone then must exist in the atmosphere, and this being allowed, we are naturally led to assume its presence, whenever those reagents which we rely upon for detecting it in an artificial mixture are affected in the same manner by the passing of air over them.

Now, paper soaked in a solution of iodide of potassium with starch is one of the most delicate of these tests; and so, likewise, is the protosulphate of manganese, which has an additional dose of oxygen communicated to it through the same agency, and hence, by the brown colour its solution obtains, indicates the presence of ozone.

Assuming, therefore, in either instance, that the intensity of the resulting colour is an index of the proportion of ozone present in the air, it has become the practice of meteorologists to

register its amount by comparing with a scale of colours the tint produced upon the paper by its exposure for a given time to the action of the atmosphere.

It has been objected, indeed, to this conclusion, that other bodies, which may be supposed to exist in the air, might produce similar reactions. Nitrous acid, for example, which we know to be generated by electrical discharges, would affect either kind of paper, and so likewise would chlorine, which in the neighbourhood of the sea at least, might be suspected to be present.

I think, however, it may be proved, that neither of these gases existed in the air, which, according to my observations, affected Schönbein's paper in the manner described.

Two tubes were attached to an aspirator by means of which 36 gallons of air were made to pass through them. Into one of these tubes was introduced a piece of Schönbein's paper, which, before the experiment was ended, had become sensibly blue; in the other was placed a slip of blue litmus paper, which, during the whole course of the experiment, was not in the slightest degree reddened, as would have been the case if an acid had been present. It, however, gradually became bleached, a well-known effect of the action of ozone upon vegetable colours.

Another similar aspirator was connected with a system of Liebig's tubes containing a solution of nitrate of silver, which would be rendered cloudy by the slightest trace of chlorine or any of its compounds; but the liquor remained perfectly limpid and transparent to the last.

Even admitting, therefore, that some uncertainty may attach to the validity of Schönbein's paper as indicative of the presence of ozone, when not corroborated by other independent tests, I am at a loss to what other cause to attribute the change of colour occurring after exposure to the air, when proper care has been taken to exclude *direct sunlight*, which, as will be stated hereafter, seems alone sufficient to separate iodine from its combinations, so as to produce the blue colour with starch.

Now it may be taken for granted, that any principle generally diffused throughout the atmosphere must have some special uses assigned to it in the economy of nature, and hence it becomes a matter of interest to the meteorologist, as well as to the chemist, to register the relative proportion in which ozone presents itself at different times and places, so as to determine, if possible, the conditions upon which its appearance depends.

I have, therefore, been induced for some time past to note down, at intervals of twelve hours, by reference to a scale of colours, the amount of ozone assumed to be present in the atmosphere, during the winter season at Torquay, and during the rest of the year at Oxford, registering in each case the direction of the wind at the time being, and other meteorological conditions.

The following summary of the results obtained during 1864, 1865, and 1866, at Torquay, may lead to some inferences as to the dependence of the amount of ozone upon the direction of the wind, at least at that part of England.

1864.

In the month of February.

Total amount of ozone was 230
Average per day ..... 8·2

Wind.	Days.	Ozone.	Average.
W.	5	70	14·0
S.W.	2	28	14·0
N.E.	7	65	9·3
S.	4	36	9·0
E.	3	22	7.3
N.W.	2	5	2·5
N.	2	4	2·0

In March.

Total in the month ..... 293·0
Average per day ..... 8·3

Wind.	Days.	Ozone.	Average.
S.	4	52	13·0
W.	11	122	11·0
S.W.	1	11	11·0
N.W.	2	16	8·0
E.	4	28	7·0
S.E.	1	6	6·0
N.E.	7	38·5	5·5
N.	4	22·0	5·5

1865.

January, at Torquay.

Total of ozone 160

Average..... 5·1

Wind.	Days.	Total of Ozone.	Average.
S.	1	10	10
W.	6	53	8·8
S.W.	1	6	6·0
S.E.	2	12	6·0
N.W.	8	44	5·5
N.	4	17	4·25
E.	5	12	2·40
N.E.	4	6	1·50

February, at Torquay.

Total of ozone 266

Average..... 9·5

Wind.	Days.	Total of Ozone.	Average.
E.	1	15	15·0
W.	7	91	13·0
S.	3	30	10·0
S.W.	7	66	9·4
N.W.	3	25	8·3
N.E.	4	32	8·0
S.E.	1	3	3·0
N.	2	4	2·0

March, at Torquay.

Total of ozone 222

Average..... 7·16

Wind.	Days.	Total of Ozone.	Average.
S.	2	25	12·5
W.	4	48	12·0
S.W.	2	19	9·5
N.E.	4	38	9·5
S.E.	3	22	7·3
N.W.	6	39	6·5
E.	3	18	6·0
N.	7	13	1·85

1866.

January, at Torquay.

Total of ozone ..... 220·0

Average..... 7·0

Wind.	Days.	Total of Ozone.	Average.
N.E.	1	13	13
E.	1	12	12
S.W.	7	69	9·8
W.	7	59	8·4
N.W.	5	37	7·4
S.	2	13	6·5
S.E.	2	10	5·0
N.	6	7	1·1

February, at Torquay.

Total of ozone..... 169

Average 6

Wind.	Days.	Total of Ozone.	Average.
S.W.	5	47	9·4
W.	10	81	8·1
N.W.	6	37	6·1
N.	6	4	·6
N.E.	1	0	·0

March, at Torquay.

Total of ozone..... 201

Average ..... 6·4

Wind.	Days.	Total of Ozone.	Average.
S.W.	1	15	15
S.	1	12	12
S.E.	4	48	12
N.W.	6	41	6·8
W.	8	54	6·7
E.	1	6	6·0
N.E.	3	12	4·0
N.	7	22	3·1

The following is a summary of the results :—

Table I.

Average Amount of Ozone during two months in 1864, *three months in* 1865, *and three months in* 1866, *at Torquay.*

	W.	S.W.	N.E.	S.	E.	N.W.	N.	S.E.
1864.								
February....	14·0	14·0	9·3	9	7·3	2·5	2	0
March.....	11·0	11·0	5·5	13	7	8	5·5	6
1865.								
January	8·8	6·0	1·5	10	2·4	5·5	4 25	6
February....	13·0	9·4	8·0	10	15	8·3	2·0	3·0
March.....	12·0	9 5	8 5	12 5	6	6·5	1·85	7·3
1866.								
January	8·4	9·8	13·0	6 5	12·0	7·4	1·1	5·0
February....	8·1	9·4	0	0	0	6·1	0·6	0
March.....	6·7	15·0	4 0	12·0	6·0	6·8	3·1	12·0
Total	82·0	84·1	49·8	73 0	55·7	51·1	20·4	39·3

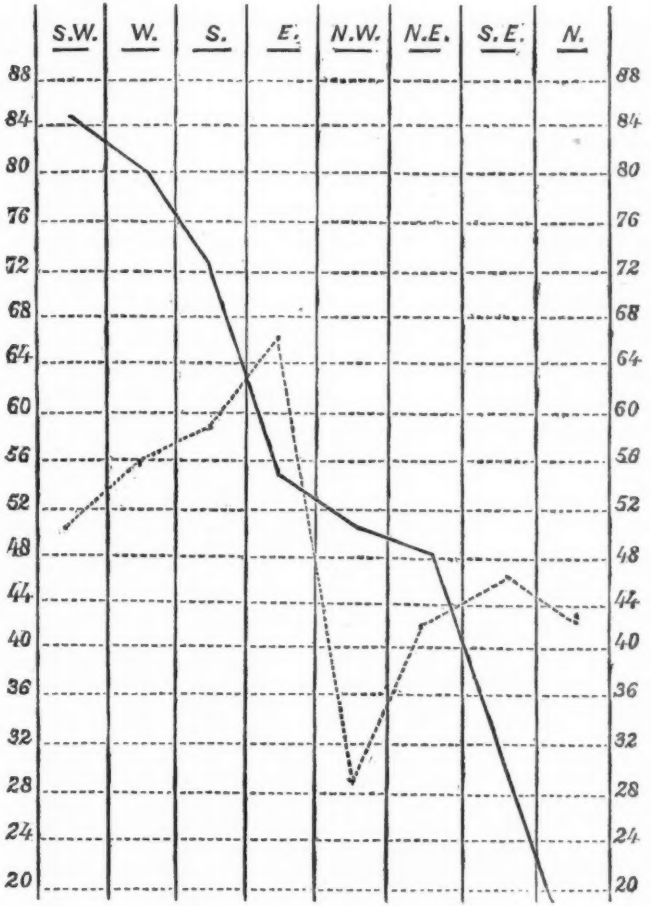
From this it would appear that in Devonshire there is, on an average, most ozone when the wind is blowing from the south-west and west, the numbers representing each of these nearly corresponding; that the next in efficacy as a carrier of ozone is the south; that the east, north-east, and north-west come lower still, but are nearly alike in this respect; that the south-east stands still lower; and that the north is lowest of all, its quality as a carrier of ozone being to that of the south-west wind only as 20 to 84, or less than one-fourth.

But when I compared these observations with those undertaken at Oxford during the same period of time, although at a different season of the year, I found that the same law does not obtain.

From the table drawn up as the result of my ozone observations during the months of May, June, and August, 1865, and of April, May, June, and July, 1866, in which the average amount of ozone for each day during which the wind blew in a certain direction was noted, it appears that whilst the average amount of ozone per month at Torquay was 58·0, that at Oxford was only 43·3, and moreover, that whilst at the former place the largest amount occurred during the prevalence of the south-west winds, and the least during that of the north; at Oxford, on the contrary, the east wind stands highest of all in its ozone-bearing properties,

and the north-west lowest; whilst the difference between the respective winds in this respect did not exceed 5 to 2; instead of 4 to 1, as at Torquay.

In the following diagram the variations in the amount of ozone according to the direction of the winds are noted, those at Oxford being indicated by a dotted, those at Torquay by a continuous line, from which it appears that there is no correspondence in this respect between the two places.



In drawing conclusions, however, from the above premises, it must be confessed that some caution must be exercised; for it is evident that two causes might influence the results, and thereby

render uncertain the quantitative estimation of the ozone by the method described.

The first of these is the influence exerted by light upon the coloration of the exposed paper, a point upon which I shall afterwards say more.

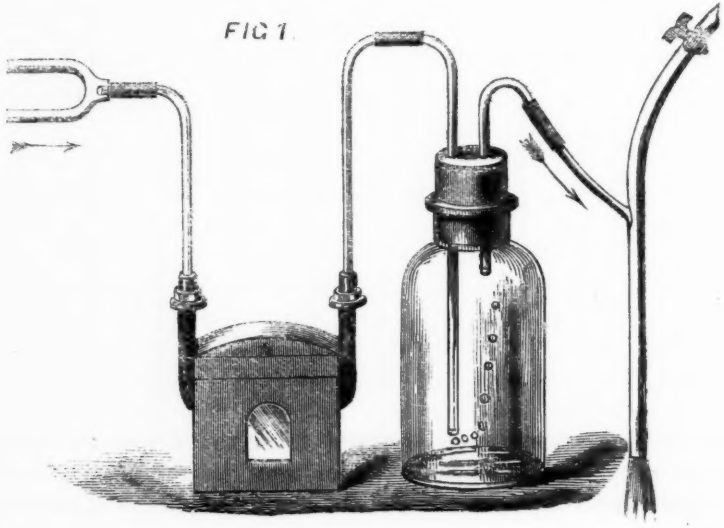
The absence, indeed, of any coloration of the paper for several days together, as shown by the register, proves that the situation selected was sufficiently protected from strong light to prevent the paper from being much affected by this cause, for certainly the paper was sometimes least changed when the day was brighest.

Still, however, a part of the result may have been due to this influence, as I have found a difference in the amount of coloration between paper placed in a tube blackened externally, and in one freely admitting diffused light.

Another source of uncertainty arises from the difference in the force of the wind at one time and another. It is evident that this circumstance must influence materially the amount of ozone which acts in a given time upon the paper exposed to its influence; and hence, as in the south-west of England, some of our most violent gales proceed from that quarter, it may be said, that the greater amount of coloration observed was due to the force of the wind, and not to its direction.

I have lately constructed an apparatus (fig. 1), by means of which this cause of uncertainty may, I conceive, be eliminated,

FIG 1.



as the air is made to pass through the tube containing the ozone paper at a certain definite rate, as measured by a gas-meter in connexion with the aspirator beyond.

The apparatus has not been, as yet, employed sufficiently to allow of my reporting the results, but in the meantime I may remark, that although the objection stated might be apt to shake our confidence in any small number of observations, yet when the latter are extended over many months, and indicate a difference so great as that from 84 and 82 to 33 and 20 between the ozonizing influence of the west and south-west winds, as compared with that of the south-east and north, it seems impossible to attribute the whole to the force of the respective winds, or to deny that the results afford countenance to the idea, that as the south-west, west, and south winds come chiefly from the ocean, whilst the north blows over a wide expanse of land, and the south-east proceeds from the continent of Europe, with a short tract of sea only intervening, the small quantity of ozone detected in the latter cases may be partly due to the wider surface of land which they had traversed, before coming into contact with the paper.

Assuming, therefore, as a fact, a variation in the quantity of ozone at different times and places, it will be interesting, with a view of understanding how it originates, to consider two points: first, in what manner does ozone originate; and, secondly, what uses it subserves in the economy of nature.

With respect to the former of these questions, it has been suggested as probable, that in every case in which oxygen is disengaged from its combination with a base, ozone may be generated. Thus Sir Benjamin Brodie informs me that he found it abundantly evolved during the decomposition of carbonic acid, when carbonic oxide and oxygen were produced simultaneously by electrolysis. Thus, if sulphuric acid be added to a solution of permanganate of potassa, ozone continues to be liberated for a considerable time, until the whole of the permanganate has been decomposed.

Thus, when water is decomposed by electricity, ozone is sometimes liberated at the oxygen pole, as may be seen by introducing a slip of Schönbein's paper into the gas disengaged.

As, therefore, the principal agent for restoring oxygen to the atmosphere when vitiated by animal processes is vegetation, we might naturally expect that ozone should be disengaged by the leaves of plants during their exposure to sunlight.

Nevertheless, Dr. Gilbert, in his researches on the sources of

the nitrogen absorbed by plants, denies that any ozone was present in the air he collected from leaves immersed in water impregnated with carbonic acid gas during sunshine; and I have myself made a number of experiments this summer bearing upon the same point, in none of which I was able to discover evidence of any ozone in the gas collected from leaves, although the proportion of oxygen present in it was sufficient to rekindle a red-hot match.

I also modified the experiment by placing tubes filled with common air over jars containing water, into which fresh leaves were introduced, and exposed them to the solar light, expecting that if any ozone were generated, it would become discoverable by diffusing itself through the air of the tube in connection with the jar.

But here I was also disappointed in obtaining satisfactory results, the only cases in which the paper was affected being those in which light had been allowed to come into contact with the air of the tube.

Now, I have found that the direct rays of the sun are capable, by themselves, of decomposing iodide of potassium, and thus of producing a blue tint on Schönbein's paper; and, moreover, that Moffat's becomes speedily changed under the same influence. Even diffused light accelerates the action of ozone upon the paper, although it does not seem able by itself, within any limited time, to produce the chemical change, as it has frequently occurred to me, to find paper remain unaltered for days together after free exposure to the air in the shade.

The following table will show that paper wholly protected from light is less affected than the same contained in a tube to which light was admitted, but still that even in the former case a certain influence was exerted by the ozone present.

Table II.

Experiments performed during the day, but in the shade.

	Tube blackened.			Not blackened.		
	Hours.			Hours.		
	4	8	12	4	8	12
July.						
14	0	0	0	4	4	5
15	0	0	2	0	3	3
16	0	0	0	0	2	2
17	0	2	2	2	2	3
18	0	0	0	1	1	1
19	0	1	2	2	2	3
20	0	0	0	0	0	2
21	0	0	0	0	1	3
24	0	0	0	0	0	0
25	0	0	0	0	0	0
26	0	0	2	0	1	4
27	0	0	1	0	1	3
28	0	0	3	0	3	5
29	1	2	3	3	4	6
30	3	3	4	2	4	7
31	0	2	2	1	3	4
August.						
1	1	1	1	3	3	4
2	0	0	2	1	2	3
3	0	1	3	0	2	4
4	0	2	3	2	3	5
5	0	1	1	1	2	3
6	0	2	3	1	4	6
7	1	2	4	2	3	6
8	2	3	4	3	4	6
9	0	0	0	0	0	0
10	1	1	4	3	4	5
11	1	3	4	4	5	7
12	0	0	2	0	3	4

It is, therefore, always necessary, when observations on the presence of ozone in air are taken, not only to provide that the paper should be well screened from direct light, but also that the amount of coloration due to that diffused should be allowed for, by comparing the tint produced under this condition with that obtained from the same paper placed in the dark.

By attending to these precautions, I think myself warranted in concluding, that ozone is really disengaged by the green parts of plants, for when I conducted the experiments in a different manner from that in which they were carried on by Dr. Gilbert, I produced a degree of coloration upon Schönbein's papers which does not seem attributable to any other cause.

In the experiments now alluded to, the whole plant, or a portion of it, was covered over by a jar, having suspended in it one or more slips of Schönbein's paper in immediate juxta-position, but not in actual contact with the plant, and a rapid circulation of air through the jar was prevented by attaching a piece of porous paper loosely to the open extremity of the vessel. The papers were examined at intervals of 1, 3, 6, and 9 hours, and the amount of coloration, if any, was recorded.

As the admission of a certain amount of solar light to the plant constituted the very condition of the experiment, it was necessary to eliminate the effect due to the action of this agent upon the paper, from that produced by the mere disengagement of ozone from the plant, and for this purpose a jar with a piece of Schönbein's paper suspended in it was exposed to the sun under the same conditions as in the former instance, except that no plant was introduced. At the same time a jar containing a similar slip of paper was placed near the others, protected from the sun's light by a dark shade, in which case it was inferred, that any coloration which might take place would simply be due to the ozone floating in the atmosphere, and thus that the effect attributable to the latter might be estimated and allowed for.

The following are a few of the general results deduced from the experiments I made, of which tabular view is given :—

Table III.

Experiments upon the effects of the Leaves of Plants during sunshine upon Schönbein's Iodised Paper.

No.	Family.	Name of Plant.	Date.	Time of Exposure.	Degree of Coloration.			Circumstances of the Weather, &c.
					When the paper was placed over the plant.	When the paper was apart from the plant.		
						Exposed to light.	In the dark.	
				Hours.				
1	Acanthaceæ	Acanthus speciosus	June 23rd	1	3	3	0	Sun bright. Wind E. Ozone in the open air in 24 hours = 4. Th. max. 72, min. 52
				3	7	3	1	
2	Araliaceæ	Aralia racemosa	June 28th	3	2	0	0	Sun bright. Wind N. Ozone = 12. Th. max. 78, min. 50
				6	8	4	2	
3	Aristolochiaceæ .	Aristolochia clematitis ...	May 28th	6	4	..	..	Day cloudy. Wind W.; high. Oz. 11. Th. max. 67, min. 42
4	Balsamineæ	Impatiens parviflora.....	June 16th	1	4	1	0	Sun bright. Wind W.; high. Oz. 0. Th. max. 61, min. 50
5	Berberideæ.....	Berberis iberica	June 29th	3	0	2	0	Sun bright. Wind N., high. Oz. 8. Th. max. 77, min. 60
				6	2	3	1	
6	Borragineæ.....	Symphytum asperrimum .	June 26th	1	1	0	0	Day fine and bright. Wind N.E. to E. Oz. 10. Th. max. 76, min. 57
				3	3	2	0	
				6	4	4	1	

TABLE III—*continued.*

No.	Family.	Name of Plant.	Date.	Time of Exposure.	Degree of Coloration.			Circumstances of the Weather, &c.
					When the paper was placed over the plant.	When the paper was apart from the plant.		
						Exposed to light.	In the dark.	
				Hours.				
7	Campanulaceæ .	Campanula alternifolia...	June 4th	1	3	1	0	Day cloudy; warm. Wind S.E. to
8	..	Phyteuma campanuloides.			3	1	0	W. Oz. 5. Th. max. 68, min. 57
9	Caprifoliaceæ...	Symphoria racemosa	June 30th	3	3	1	0	Day fine. Wind S. Oz. 10. Th.
				6	3	4	1	max. 77, min. 50
10	Caryophylleæ...	Saponaria officinalis	June 22nd	1	5	3	0	Day fine. Wind N.W. Oz. 3. Th. max. 70, min. 57
11	Cornaceæ	Cornus alba	June 29th	3	2	2	0	See No. 5
				6	2	3	1	
12	Cruciferæ	Lepidium latifolium	May 28th	6	8	..	..	See No. 3
13	Compositæ	Balsamita vulgaris	May 29th	6	5	2	1	Day fine; cloudy. Wind N. Oz. 3. Th. max. 62, min 45
14	..	Cacalia suaveolens.....	May 31st	4	3	3	0	Day fine. Wind E. Oz. 10. Th.
				8	2	3	1	max. 64, min. 49
			June 2nd	1	2	1	0	Sun bright; thunder showers.
				3	2	2	1	Wind E. Oz. 8. Th. max. 69,

				6	4	3	0	min. 51
				9	4	2	0	
15	..	Calendula officinalis	June 16th	1	3	1	0	See No. 4
16	..	Hieracium humile	May 28th	6	4	1	0	See No. 3
			May 31st	4	0	3	0	See No. 14
				8	5	3	1	
17	..	„ rupestre	May 29th	6	5	2	1	See No. 13
18	..	Rudbeckia subtomentosa..	May 29th	6	7	2	1	Ditto
19	..	Solidago elliptica.....	May 29th	6	6	2	1	Ditto
			May 31st	4	4	3	0	See No. 14
				8	6	3	1	
20	..	„ latifolia	May 31st	4	3	3	0	Ditto
				8	7	3	1	
21	Coniferæ	Pinus excelsa	May 29th	6	3	2	1	See No. 13
			May 31st	4	0	3	0	See No. 14
				8	3	3	1	
			June 2nd	1	4	1	0	See No. 15
				3	4	2	1	
				6	3	3	0	
				9	3	2	0	
22	Cucurbitaceæ...	Momordica elaterium	June 28th	3	4	0	0	See No. 2
				6	4	4	2	
23	Dipsaceæ.....	Scabiosa sylvatica	June 28th	3	4	0	0	See No. 2
				6	4	4	2	
24	Eleagneæ	Eleagnus augustifolia	June 29th	3	4	2	0	See No. 5
				6	5	3	1	
25	Ericaceæ.....	Rhododendron positicum .	June 23rd	1	1	3	0	See No. 1
				3	1	4	0	

TABLE III—*continued.*

No.	Family.	Name of Plant.	Date.	Time of Exposure.	Degree of Coloration.			Circumstances of the Weather, &c.
					When the paper was placed over the plant.	When the paper was apart from the plant.		
						Exposed to light.	In the dark.	
26	Gentianeæ	Pneumonanthe acaulis ...	June 30th	3	2	1	0	See No. 9
				6	2		1	
27	Gramineæ.....	Hierochloe borealis	June 26th	1	1	0	0	See No. 6
				3	3	2	0	
				6	3	4	1	
28	Grossulariceæ ...	Ribes sanguinea	June 28th	3	0	0	0	See No. 2
				6	3	4	2	
29	Labiatæ.....	Mentha crispa	June 4th	1	2	1	0	See No. 7
30	Leguminosæ....	Ulex europæus.....	May 28th	6	6	..	..	See No. 3
31	Lobeliaceæ	Lobelia tupa.....	June 30th	3	4	1	0	See No. 9
				6	6	4	1	
32	Lythrarieæ	Lythrum virgatum	June 23rd	1	3	3	0	See No. 1
				3	6	4	0	
33	Malvaceæ	Althæa rosea	June 16th	1		1	0	See No. 4
34	..	Lavatera olbia	June 26th	1	1	0	0	See No. 6

				3	3	2	0	
				6	4	4	1	
35	Nyctagineæ	Oxybathus violaceus	June 23rd	1	3	3	0	See No. 1
				3	3	4	0	
36	Oleaceæ.....	Ligustrum vulgare	June 26th	1	0	0	0	See No. 6
				3	2	2	0	
				6	4	4	1	
37	Onagrariæ.....	Chamœnerion rosmarinifolium	June 23rd	1	3	3	1	See No. 1
				3	4	4	0	
38	Papaveraceæ..	Papaver somniferum	June 22nd	1	1	3	0	See No. 10
39	Plumbagineæ ..	Plumbago europœa	June 22nd	1	6	2	0	See No. 10
				3	3	3	1	
40	Polemoniaceæ ..	Collomia grandiflora	June 16th	1	2	1	0	See No. 4
41	Polygoneæ	Polygonum divaricatum ..	June 4th	1	3	1	0	See No. 7
42		„ cymosum	Do.	1	2	1	0	
43	Ranunculaceæ ..	Helleborus fœtidus	June 26th	1	1	0	0	See No. 6
				3	2	2	0	
				6	4	4	0	
44	Resedaceæ	Reseda luteola	June 22nd	1	2	3	0	See No. 10
45	Rosaceæ	Potentilla anserina	June 22nd	1	3	3	0	See No. 10
46	Rutaceæ	Dictamnus fraxinella	June 23rd	1	1	3	0	See No. 1
				3	6	4	0	
47	Salicineæ	Salix alba.....	June 30th	3	2	1	0	See No. 9
				6	4	4	1	
48	Saxifrageæ	Astilba rivularis	June 28th	3	3	0	0	See No. 2
				6	3	4	2	

TABLE III—*continued.*

No.	Family.	Name of Plant.	Date.	Time of Exposure.	Degree of Coloration.			Circumstances of the Weather, &c.
					When the paper was placed over the plant.	When the paper was apart from the plant.		
						Exposed to light.	In the dark.	
				Hours.				
49	Scrophularineæ .	Phygelius capensis	June 23rd	1	2	3	0	See No. 1
				3	4	4	0	
50	Simarubeæ	Ailanthus glandulosa	June 30th	3	4	1	0	See No. 9
				6	6	4	1	
51	Solaneæ.....	Physochlæna orientalis ..	June 23rd	1	1	3	0	See No. 1
				3	3	4	0	
52	Tiliaceæ.....	Tilia europœa	June 29th	3	3	2	0	See No. 5
				6	3	3	1	
53	Tropœoleæ	Tropœolum majus	June 16th	1	2	1	0	See No. 4
54	Ulmaceæ	Ulmus montana	June 29th	3	1	2	0	See No. 5
				6	5	3	1	
55	Umbelliferæ....	Meum athamanticum	June 22nd	1	1	3	0	See No. 10
56	Urticaceæ.....	Urtica canadensis.....	May 29th	6	5	2	1	See No. 13
57	Violaceæ	Viola grandiflora.....	June 23rd	1	1	2	0	See No. 1
				3	1	3	1	

From this table it will be seen that the experiments were tried upon fifty-seven species of plants belonging to forty-seven natural families.

In thirteen of these cases the coloration produced upon paper introduced into the jar containing the plant, was less in degree than that occasioned by light upon the same suspended in an empty jar for the same period.

But in thirty-two cases the reverse was observed, the degree of coloration attributable to the plant being sensibly greater.

In all, however, the coloration of paper placed in a darkened jar was much less considerable than in one freely exposed to light; indeed, in most instances, the paper remained uncoloured, and in none, even after six hours' exposure, did it exceed 2° of the scale.

The highest amount of coloration due to mere light was, after one hour's exposure, = 3; after six hours, = 4. This occurred in each case nine times.

Now in the jars containing a growing plant, the coloration of the paper in an hour amounted in one case to 5°; in two cases to 4°; in seven cases to 3°; in four cases to 2°; in four to 1°; and in three only to none at all.

In a few cases the coloration went on increasing from the first hour to the third, and even to the sixth; but never at any regular rate of progression. Thus *Solidago latifolia* in one hour produced a coloration = 4°; and in six hours one of 6°.

Hieracium rupestre in one hour produced 4°; in three hours, 5°; in six hours, 6° of coloration; whilst paper in a jar exposed to the same amount of sunlight, without access to a plant, was coloured in one hour, 1°; in three hours 2°; and in six hours 3°.

On the other hand the leaves of *Pinus excelsa*, which in one hour gave a coloration to paper amounting to 4°, produced no deeper tint in three hours; and in six hours the colour of the paper had sunk to 3° of the scale, at which point indeed it remained after 9 hours' exposure.

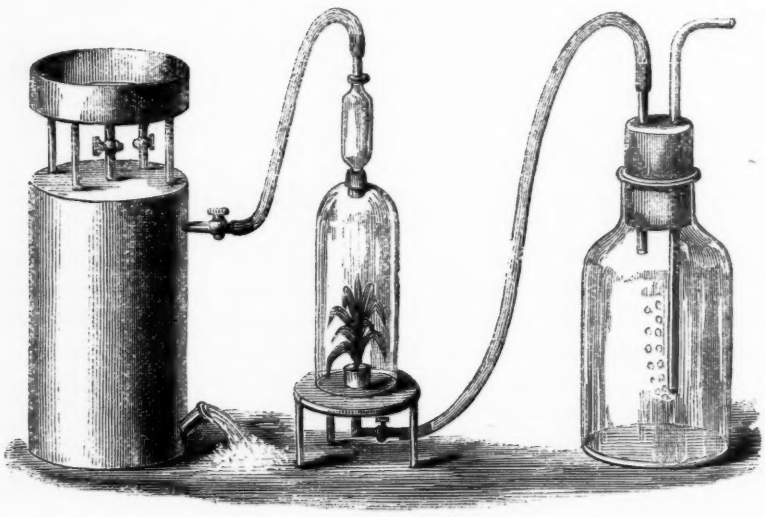
Other anomalies of an equally striking character may be observed on consulting the tabulated results, and they seem only explicable by considering, that owing to the volatile nature of iodine, a portion of that disengaged from its combination by the ozone present is constantly becoming dissipated, so that the amount of coloration is an *index*, not of the quantity of iodide of potassium decomposed during the time the experiment had been continued, but only of the ratio between the oxidizing action

which sets the iodine free, and the tension of the latter, which causes it to evaporate into space.

Something may also be due to the bleaching effect which ozone exerts upon vegetable colours, owing to which the blue tint of the combination between the iodine and the starch may be discharged shortly after its formation; and a further source of uncertainty may arise from the presence of ozone in the atmosphere at the time being, which would influence the paper in the same manner as that disengaged from the plant.

With the view of eliminating, so far as possible, these several sources of error, and of determining what part of the effect observed was really due to the ozonizing influence of the leaves, I devised the following form of apparatus:—

FIG. 2



A jar having a wide tube open at both ends ground into its tubulure, was placed over a growing plant, and rested upon a ground brass plate, to which it could be fixed nearly air tight.

A flexible tube screwed into the brass plate allowed air to enter the jar from without, and a similar one was attached to the upper end of the tube, communicating with an aspirator, by which air could be drawn continuously through the jar. The air that entered

the jar was, however, deprived of ozone by being made to pass through a washing bottle containing iodide of potassium and a little starch, which by its coloration would indicate when the liquid was saturated, and moreover, before entering the jar, the air, after passing through the washing bottle, was made to come in contact with a slip of Schönbein's paper, placed in an intervening tube.

Similar slips were placed in the jar in near proximity to, but not in contact with the plant, as well as in the tube above, a part of which was exposed to light, whilst the rest was covered with black paper for the purpose of excluding it.

After several hours' exposure to light, and after passing through it from 24 to 30 gallons of air, the plant was removed, and the papers examined.

The following were the results obtained in five experiments conducted in this manner:—

1st. Experiment with a small plant of *Veronica salicifolia*.

Duration of the experiment.	Air passed through jar.	Paper.		
		In the jar.	In the upper tube.	
			Part exposed to light.	Part darkened.
10 hours	27 gall.	Coloured to 5 of scale.	4	3

I should infer from this that sufficient ozone had been generated by the plant to produce a coloration equal to 5°.

2nd. Experiment on a variety of Cape Pelargonium.

Duration of experiment.	Air drawn through the jar.	Paper.		
		In the jar.	In tube exposed to light.	In tube darkened.
10 hours	30 gall.	3	3	1

The day was overcast, and therefore less favourable to the experiment than the preceding one had been.

3. Experiment with *Chrysanthemum sinense*.

Duration of experiment.	Air passed through the jar.	Paper.		
		In the jar.	In tube when exposed to light.	In tube when darkened.
10 hours	30 gall.	2	2	1

Here, therefore, the paper placed in the darkened portion of the tube would seem to indicate the amount of ozone due to the plant.

Experiment 4, with *Phytolacca decandra*.

Duration of experiment.	Quantity of air drawn through.	Paper.		
		In the jar.	In tube where light entered.	When darkened.
8 hours	30 gall.	Owing to the paper being placed so close to the plant as to be wetted by its moisture, no coloration.	4	2

Here, although the accident pointed out prevented the paper in the jar from showing any effect, there would seem to have been ozone enough generated to produce a coloration of 2° in the darkened portion of the tube above.

Experiment 5, on a *Convolvulus*.

Duration of experiment.	Quantity of air drawn through.	Paper.		
		In the jar.	In tube.	
			Exposed to light.	Darkened.
9 hours	24 gall.	5	5	2

Upon the whole, then, I felt myself warranted in concluding that, inasmuch as, although ozone had been excluded by the method described, the paper introduced into the tube placed over the plant

was in every instance affected, the quantity of this ingredient generated by the plant itself might be estimated by the degree of coloration which had taken place in the paper placed in the darkened portion of the tube.

After the above experiments had been in a great degree completed, I found, by turning to the 18th volume of the 4th series of the "Annales des Sciences Naturelles," that I had been anticipated in the conclusions arrived at by M. Kosmann, of Strasburg, who, from a series of not less than 253 observations, had felt himself warranted in inferring, that Schönbein's papers placed over growing plants are more deeply affected in a given time, than others left in contact with the open air at a distance from all vegetation.

As, however, this gentleman seems to have taken no further precautions than that of freely suspending the paper, in the open air, over the plants in the one instance, and at a distance from them in the other, it may not be thought, that the experiments which I have detailed, in which steps were taken to prevent any ozone from reaching the paper, except from the plant itself, are altogether thrown away with reference to the establishment of the conclusion arrived at.

With regard to the absence of any coloration, when paper was exposed to the action of the gas given off by leaves immersed in water, an explanation may be found in the readiness with which ozone is destroyed by any kind of organic matter.

The latter would doubtless exist floating in water in which leaves had been immersed, and would thus prevent any ozone generated by the plant from rising into the tube fixed into the tubulure of the jar containing the leaves. Indeed, in several experiments, which I do not detail, as their results were vitiated by this cause, I found that the mere transmission of the ozone through a caoutchouc tube was sufficient to cause its disappearance.

The want of any definite relation between the intensity of colour and the time of exposure, may be referred to the volatility of the iodine, and its consequent escape, so that it might easily happen, that if the evolution of ozone did not proceed at an uniform rate, the coloration of the paper would become less instead of greater during the latter hours of the experiment. Indeed I have found in some cases, that the paper returned, after a time, almost to its original whiteness, and moreover, on days when ozone was

absent from the atmosphere, that iodised paper, rendered blue by a weak acid, would lose its colour on exposure to the air.

It must be confessed that the want of any definite rate of progression in the deepness of the tint produced upon Schönbein's paper, in proportion to the number of hours during which it had been exposed, is calculated to shake one's confidence in this test, considered as a measure of quantity. Thus the following table will represent the indications afforded during the month of July last, by paper exposed in the open air during 4, 8, and 12 consecutive hours.

TABLE IV.

Degree of Coloration produced on Schönbein's Paper on the days mentioned.

	Hours.		
	4	8	12
July 14	3	4	6
„ 15	3	3	6
„ 16	2	2	2
„ 17	2	3	3
„ 18	1	1	2
„ 19	3	3	3
„ 20	2	2	2
„ 21	1	1	4
„ 22	0	1	1
„ 23	0	0	0
„ 24	1	3	4
„ 25	1	2	5
„ 26	1	3	6
„ 27	3	5	7
„ 28	3	6	9
„ 29	4	4	5
„ 30	3	4	6
„ 31	1	2	4
August 1	3	3	4
„ 2	3	5	6
„ 3	3	3	4
„ 4	3	5	8
„ 5	3	4	8
„ 6	4	6	7
„ 7	0	0	2
„ 8	4	4	6
„ 9	4	6	8
„ 10	3	4	6

I have seen it somewhere asserted that flowers as well as leaves emit ozone, but this statement is entirely opposed, both to M. Kosmann's observations, and to my own.

In one or two cases, indeed, a certain degree of coloration was observed, but this may be referred to other causes, as in the case of the Fraxinella, to the essential oil emitted by the flower, which may have possibly affected the paper. In the majority of instances at least, the degree of coloration produced was not greater than what took place in the same paper by exposure to an equal amount of solar light where no plant was present. Considering, indeed, that the function of the flower in the vegetable economy is antagonistic to that of the leaf, the one assimilating oxygen, the other causing its emission, it could not be expected, that because ozone is generated by the organs designed for nutrition, it should therefore be emitted by those destined for reproduction.

Indeed leaves do not appear to give out ozone in the dark, or when their office of emitting oxygen is suspended, a difference which can be easily accounted for, if we consider that at these times, as I long ago pointed out in my memoir "On the Action of Light upon Plants," in the Phil. Trans. for 1836, they contribute, like the other parts of a vegetable, towards the production of carbonic acid, although not in such a degree as to compensate for the amount of this gas which they decompose during the continuance of sunlight.

May not this serve to account for the injurious effect upon the health ascribed to flowers when placed in large quantities in sleeping apartments?

This has been ascribed by some to the oxygen they consume, but their influence in this way must be wholly inappreciable. It is possible, however, that the essential oils which some flowers exhale exert a noxious effect upon the nervous system; but independently of this, they may, perhaps, render the air of inhabited places less salubrious, by co-operating with other influences which contribute under such circumstances towards the destruction of ozone.

And this leads me to the last question to be considered, namely, the uses which ozone subserves in the economy of nature.

When we consider its remarkable oxidising properties and the rapidity with which any organic matter, dead or living, undergoes a slow combustion in its presence, it seems reasonable to conclude, that this principle is an important agent for destroying putrescent animal and vegetable matter by oxidation, and thus for restoring to the atmosphere its purity.

Plants, indeed, decompose carbonic acid, and thus serve to maintain unaltered the original composition of the atmosphere; but the various products of putrefaction, the emanations from animals, living as well as dead, the exhalations from swamps and marshes, would still continue to contaminate it, were it not for the presence of some agent capable of removing these bodies from the fluid in which they are floating, and of rendering them innocuous by oxidation.

And that such a function is really discharged by ozone may be suspected, from finding traces of this ingredient in air which has blown from the sea, more generally than in that which has swept over an inhabited region, as has been already pointed out; also from recognizing it in greater abundance in the air of the country than in that of towns, and from observing that it is entirely deficient in that of inhabited rooms, even at times when it can be clearly detected outside the dwelling.

Hence it appears not improbable that the salubrity of a place depends upon the presence of ozone, which may be regarded as an *index*, at once of the absence of organic matter in the atmosphere of the place, and of the readiness with which it would be removed whenever it chanced to be evolved.

And if the observations I have brought forward, on my own authority and that of others, be regarded as sufficient to establish the fact, that the green parts of plants during the day are constantly evolving ozone, they will tend to show, that vegetation is not only, as Dr. Priestley originally pointed out, the appointed means for restoring the equilibrium of the atmosphere, but likewise the agent for destroying those impurities, which would otherwise make it unfit for the existence of the higher classes of animals, even although the proper proportion of oxygen in it were fully maintained.

It may be objected to this view, that ozone is said to be more abundant by night than by day, and in cold weather than in hot; but it must be recollected, that if light and heat stimulate those functions of plants by which it is generated, they likewise render more active those chemical processes by which new combinations are formed out of the constituents of decaying animal and vegetable matter, and that the ozone produced by vegetation or other causes is not confined to the spot where it is generated, but becomes speedily diffused through the general body of the atmosphere.

It must be regretted, indeed, that no better and more precise

mode of estimating such minute quantities of ozone has been discovered, than that of the blue tint produced upon paper moistened with a solution of starch and iodide of potassium, or the brown colour induced upon protosulphate of manganese, as in the case of that proposed by Moffat. I cannot rely upon different samples of either paper yielding, under the same circumstances, exactly similar results, and, therefore, am loth to confide in their indications as furnishing corresponding measurements.

Nevertheless, by accumulating a number of observations carried on by the same person, and under the same circumstances, and by eliminating, as I have endeavoured to do, the action due to the presence of light, I trust to having arrived at some conclusions, which may at once substantiate the reality of ozone existing as an important agent in nature, and also serve to point out one at least of the agencies by which it is supplied, as fast as it is consumed in the atmosphere, in the quantities required for the necessities of animal existence.

One of the first memoirs that I ever communicated to a scientific society was that published in the "Philosophical Transactions for 1834," in which I confirmed the original conclusions of Priestley, which had been disputed by Ellis and others, with respect to the purifying influence which plants exert upon the air, by restoring to it more oxygen by day than they consume by night, and in which I also determined the description of solar rays, which was most instrumental for that purpose—a point which, as M. Decandolle remarked in his late address to the Botanical Congress, is now regarded as having been fully substantiated by the later researches of Draper and Sachs, although I perceive it still seems to be disputed by certain philosophers. Should I now have succeeded in establishing to the satisfaction of the scientific world, that these same green parts of plants, at the very time that they are emitting oxygen, convert a portion of it into ozone, I might hope that these researches of my later years will serve appropriately to wind up those undertaken in my younger ones, by showing that vegetable life acts as the appointed instrument for counteracting the injurious effects of the animal creation upon the air we breathe, not merely by restoring to it the oxygen which the latter had consumed, but also by removing, through the agency of the ozone it generates, those noxious effluvia, which are engendered by the various processes of putrefaction and decay.

However, it may be urged by some, that it is premature to speculate as to the uses of a principle, until we are fully assured of its existence; and although it would seem extremely unaccountable, that air which had been in contact with a growing plant, should, when introduced into a darkened tube, affect Schönbein's paper in the manner described, unless ozone were present in it, still it would be more satisfactory if some other test, not liable to be affected by light, could be appealed to in confirmation of its presence. And if the suggestion of some new and improved method of determining ozone should flow from the reading of this paper, I shall deem myself amply repaid for the labour it has cost me, even though the conclusions I have sought to deduce should eventually be overthrown by other more precise methods of observation.

It is time, indeed, that the question as to the existence of ozone in the atmosphere should once for all be set at rest; for at present, whilst it is disputed by some eminent chemists, it is taken for granted by meteorologists, and thus the weather tables constructed in this and most other countries are swelled by an additional column devoted to ozone observations, which, if fallacious, should be swept away as fostering the popular belief in a non-entity; and if real, should be turned to some account by those whose business it is to investigate the unexplored properties of the atmosphere in which we live.

II.—*On the Synthesis of Butylene.*

By Ernest Theophron Chapman.

[Contribution from the Laboratory of the London Institution.]

It is now some time since Wurtz succeeded in synthetically forming amylene by the action of zinc-ethyl upon iodide of allyl. It is obvious that iodide of allyl, C_3H_5I, would be isomeric with mono-iodpropylene, and this latter compound is homologous with monobromethylene. I therefore thought it worth while to treat this latter substance with zinc-ethyl, with the idea of forming butylene.

The zinc-ethyl was contained in a tubulated retort, surrounded by ice and salt. Monobromethylene was introduced into the

retort in the state of vapour. It was at once condensed. Care was taken not to add excess of it. The retort was then removed from the freezing mixture, and gently warmed. The liberated vapours were conducted through a U-tube, surrounded by ice and salt. In this manner about three c. c. of a colourless liquid were obtained. It was introduced into a small distilling apparatus, and the boiling point carefully taken. It was found to lie between 12 and 14°. The sp. gr. of the liquid was ·739 at 0° C. A small portion of it was carefully tested for bromine by passing it over red-hot caustic lime. No bromine was detected. The remainder of the liquid was treated with bromine. The two bodies combined, with considerable evolution of heat. The operation was conducted in a long test-tube immersed in ice-cold water. The resulting product was dried and distilled. It was found to boil between 158° and 160° C., though a small portion of it had a higher boiling point. It was distilled three times to remove this trace of liquid of higher boiling point.

By this time the total amount of liquid had been reduced to little more than 1 c. c. It weighed 1·526 grammes. It was then digested with solution of caustic potash in alcohol free from chlorine. The amount of bromine which it yielded to this agent corresponded with the amount required on the assumption that we were dealing with bibromide of butylene. This substance would of course give only up one equivalent of bromine. Therefore, on distilling off the alcohol and gently igniting the residue, we should obtain a mixture of bromide of potassium and caustic potash. It was in this mixture that the bromine was determined as bromide of silver.

1·526 of substance yielded 1·326 AgBr, therefore 36·97 per cent. Br. Theoretical per centage, 37·037.

The alcohol distilled off was diluted with ice-cold water: a few drops of an oily liquid rose to the surface. This liquid, on treatment with bi-chromate of potash and concentrated sulphuric acid, yielded bromine. The reaction to which the butylene owes its existence is as follows:—

$$Zn(C_2H_5)_2 + 2C_2H_3Br = ZnBr_2 + 2C_4H_8.$$

It appears to me that this reaction will enable us to obtain the whole of the olefines, normal as well as abnormal, for it is almost certain that dibromethylene would act upon two equivalents of

zinc-ethyl, producing hexylene—a secondary hexylene, no doubt; and, in a similar manner, any other required olefine could be obtained.

III.—*The Relation between the Products of Oxidation, and the Molecular Constitution of the Bodies Oxidized.*

By E. T. Chapman and W. Thorp.

[Contribution from the Laboratory of the London Institution.]

Part II.

Glycerin and mannite:—these two substances resemble each other in many particulars. They both yield iodides of secondary alcohol-radicals when treated with hydriodic acid. These iodides in both instances yield olefines when acted upon by alcoholic solution of potash. By oxidation these olefines yield acids of lower carbon-condensation than themselves. That obtained from mannite, β-hexylene, yields, as we have already shewn, propionic, acetic, and carbonic acids. The olefine from glycerin has been shewn by M. Truchot to yield acetic and formic acids; we have oxidized it and obtained acetic and carbonic acids.

It is well known that glycerin, when heated with caustic potash, yields acetic and formic acids. We have examined the reaction, and can confirm this statement.

These acids have the same carbon-condensation as those obtained from the corresponding olefine by oxidation. Mannite, when treated with caustic potash, yields propionic, acetic, and formic acids. The following experiments enable us to confirm this result. Thirty grammes of mannite were heated with caustic potash just moistened with water. The mixture melted, turned yellow, frothed up very much, and gave off inflammable gas; the contents of the dish were then dissolved in water, and distilled with excess of sulphuric acid. Formic acid was found in the distillate. A portion of the latter was converted into baryta-salt. Per centage of Ba from mixed salts, 52·83. The remainder of the distillate was neutralized with potash, evaporated to dryness, and gently warmed

with concentrated sulphuric acid. Carbonic oxide was evolved.* The mixture was then diluted and distilled, and a portion of the distillate was converted into baryta-salts. Per cent. of Ba, 50·11, showing the presence of acetic acid, because the formic acid was destroyed, and no other acid yields a barium-salt containing more than 48·41 per cent. of barium. The remainder of the distillate was neutralized with standard solution of caustic potash, and divided into four fractions, the first three of one-fifth each, and the last of two-fifths. These different fractions were, as usual, converted into baryta-salts, and the percentages of barium they contained were determined.

Substance taken.	Ba_2SO_4 found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction $\frac{1}{5}$ ·3962	·3249	48·22	48·41	Propionic
Second fraction $\frac{1}{5}$ ·3690	·3042	48·47	,,	,,
Third fraction $\frac{1}{5}$ ·4120	·3440	49·10	intermediate	
Fourth fraction $\frac{2}{5}$ ·5382	·4902	53·55	53·726	Acetic

Fractions 1 and 2 correspond closely enough with propionic acid. Fraction 3 corresponds to propionic acid contaminated with a trace of some lower acid, acetic of course; and fraction 4 corresponds to pure acetic acid. Thus mannite also yields to this treatment acids corresponding with those obtained by the oxidation of the olefine obtained from itself.

We now proceeded to oxidize glycerin and mannite with our ordinary oxidizing mixture, bichromate of potash and sulphuric acid. In both instances a most violent reaction occurs; carbonic acid is evolved abundantly, and formic acid produced. No other acid appears to be formed. The absence of other acids was proved by our ordinary process of fractionation, and by the fact that on converting a portion of the distillate in both instances into baryta-salts, and determining the percentage of barium, the numbers obtained agreed with those required by formic acid. The results of these two experiments, the treatment with caustic potash

* This treatment with concentrated sulphuric acid does not injure any acid of the acetic series, from acetic to caproic inclusive.

and the process of direct oxidation, appear to be to a certain extent antagonistic. The latter process would lead one to believe that these two substances contain each atom of their carbon directly attached to hydroxyl and hydrogen.

We observed that mannite in acid solution decolorized permanganate of potash. It appeared therefore of interest to determine how much permanganate a given weight of mannite would decolorize. But as formic acid would probably be among the products of the action, we previously experimented on some formic acid, and found that permanganate can exist in the presence of formic acid for some hours without decomposition, provided the fluid be strongly acid with sulphuric acid. In neutral or alkaline solutions the permanganate is rapidly decolorized. If, therefore, formic acid be once produced, it would not be at once decomposed by the further action of permanganic acid.

Having ascertained the behaviour of formic acid, we proceeded to operate upon a sample of mannite in precisely the manner ordinarily employed in determining oxalic acid. At first, the solution decolorized somewhat slowly, exactly as in the case of oxalic acid; then the process rapidly quickened, and for some time the decolorization of the permanganate took place almost instantaneously; afterwards, longer and longer periods were required for the decolorization. When, after ten minutes' standing, the colour had not perceptibly decreased, the process was stopped. 0·36* of mannite dissolved in dilute sulphuric acid decolorized 214 c. c. of permanganate of potash. 100 c. c. of the permanganate solution contained 0·094504 of available oxygen, therefore the mannite had required 0·20372 of oxygen. This corresponds to 92 per cent. of the amount of oxygen required to produce formic acid.

As there was so much difficulty in marking the completion of the reaction, and as the permanganate solution was much more rapidly decomposed when concentrated than when dilute, we devised a modification of the experiment. More than sufficient permanganate of potash was introduced into a flask, along with dilute sulphuric acid, and a weighed quantity of mannite added. After ten minutes, oxalic acid was added in more than sufficient quantity to decolorize the excess of permanganate employed. Then the excess of oxalic acid was in its turn determined by per-

* 1·08 of mannite was dissolved in 150 c. c. of water, and $\frac{1}{3}$ of the solution employed in each experiment.

manganate. The result of this roundabout experiment was, that a little more oxygen was employed than would have been required if the whole of the mannite had been converted into formic acid.

0·36 of mannite, dissolved in dilute sulphuric acid, was treated with 300 c.c. of the above-mentioned permanganate solution. It was allowed to stand ten minutes. A known excess of oxalic acid was then added, which immediately caused the fluid to become colourless and clear. The amount of oxalic acid in the fluid was then determined by the addition of permanganate. It appeared that 238 c. c. of permanganate had been required by the mannite. Another such experiment was made, with the exception that the liquid was allowed to stand fifteen minutes before the addition of oxalic acid, instead of ten. In this case 241 c. c. of permanganate were required by the mannite.

From the first experiment, it appears that 102·26 per cent. of the amount of oxygen required to convert mannite into formic acid was actually consumed in the operation. In the second experiment, in which the action had been allowed to continue half as long again, 103·6 per cent. of the required amount of oxygen was actually consumed.

These differences between the numbers found and those calculated are very trifling, and are amply accounted for by the slow action of permanganate upon formic acid. In order that no doubt whatever might rest upon the subject, the formic acid was actually distilled out of the mixture remaining after these operations. From it were obtained the well-known actions of formic acid. A portion of it was converted into a baryta-salt and the percentage of barium determined.

0·3402 of the salt yielded 0·3468 of sulphate of baryta; therefore 59·93 per cent. of barium. Theoretical percentage, 60·30.

Therefore mannite is decomposed by nascent oxygen, thus :—

$$C_6H_{14}O_6 + 7O = 6CH_2O_2 + H_2O.$$

IV.—*On a Chlorsulphide of Carbon.*

By Walter Noel Hartley.

In the preparation of a large quantity of dichloride of carbon or tetrachlorethylene, a solution of hydropotassic sulphide was used

for reducing the terchloride of carbon, according to the following equation:—

$$C_2Cl_6 + 2KHS = C_2Cl_4 + 2KCl + H_2S + S.$$

The mode of operation was as follows:—To a mixture of the di- and terchlorides, which contained as an impurity the protochloride of carbon, was gradually added the reducing agent prepared by dissolving potash in absolute alcohol and passing sulphuretted hydrogen through to saturation; after warming slightly, the reaction ceased, and the reduced chloride of carbon was precipitated by water from its solution in the alcohol, separated and distilled. There was a residue in the retort after distillation, which had a brown colour and a remarkable smell, suggestive of a sulphur compound. For examination, a portion was heated in a test-tube, and the result was a sublimate of sulphur and fine needle-shaped crystals. On digestion in alcohol, the substance proved to be soluble, and left on evaporation a deposit of brownish crystals. To purify this substance, it was boiled in a flask with much alcohol and animal charcoal, an inverted condenser being attached to prevent the waste of alcohol; the liquid after about four hours was filtered hot and allowed to cool in a porcelain basin; the crystals were separated; and the alcohol was used again to extract what yet remained in the flask; a fresh crop of crystals formed, and the alcohol, with a little added to it, was used again and again until the solid residue was exhausted. The substance, not yet quite pure, was again treated with alcohol and charcoal, and the filtrate was allowed to evaporate spontaneously. The resulting crystals, slightly yellow in colour, were dried under the air-pump and submitted to analysis. The specimen being only small, as little as possible was used.

0·109 grms. burnt with chromate of lead, gave 0·0519 grms. of carbonic acid, corresponding to 0·0141 grms. of carbon, or 12·93 per cent.

0·115 grms. were burnt in a small combustion-tube with pure quicklime, and oxygen was passed through the tube; it was then, while hot, dipped cautiously into water as in an ordinary chlorine determination, and treated with nitric acid. The solution yielded with nitrate of baryta 0·424 grms. of sulphate, corresponding to 0·058 grms. of sulphur, or 50·43 per cent.

On treating with nitrate of silver, the filtrate yielded 0·17

grms. of chloride of silver, corresponding to 0·042 grms. of chlorine, or 36·52 per cent.

	Found by analysis.	Calculated for the formula $C_2Cl_2S_3$.
C	12·93 per cent.	12·56
Cl	36·52 „	37·17
S	50·43 „	50·26
	99·88 „	99·99

The formula deducible from these data is, then, $C_2Cl_2S_3$, the name applicable under these circumstances being chlorsulphoform, a body of the composition $C_2H_2S_3$, being already known and called sulphoform, it being chloroform in which sulphur replaces chlorine.

Chlorsulphoform crystallises from solutions and by sublimation in fine needles, possessing a disagreeable and peculiar smell, soluble in alcohol and ether with difficulty; easily soluble in chloroform, the bisulphide, and the liquid chlorides of carbon, and in oil of turpentine. Its melting-point is not below 250° C., and it begins to sublime before it melts. When it is treated with moderately strong nitric acid in sealed tubes, for three or four hours at 120° to 130° C., white crystalline scales are formed, of which I had not enough for analysis, but from their containing sulphur, which fact I proved, and the nitric acid containing sulphuric acid, they may be regarded as a substance with, perhaps, this formula, $C_2Cl_2SO_2$. The formation of the chlorsulphoform can be in no way explained, except by supposing that the sulphur, produced in the reducing process, just as it gains its state of freedom, combines with the protochloride of carbon (C_2Cl_2). Facts support this idea: for if there be no C_2Cl_2 in the mixture to be reduced, none of the new compound is formed, and unless much sulphur be separated in the reaction, we find the C_2Cl_2 unacted upon; a solution of the hydropotassic sulphide alone has no action on it. I do not know that any other substance has been obtained by the action of nascent sulphur; if not, this may be the first instance of the formation of a compound being attributed to such an agent. The subject of this paper is part of an unfinished research upon which I was working last year in the laboratory of Professor Kolbe.

V.—*On a New Class of Compounds containing Nitrogen, in which Hydrogen is replaced by Nitrogen.*

By Peter Griess.

[Abstracted, by the Author, from the Philosophical Transactions for 1865.]

All the different nitrogen-substituted compounds that I have studied up to the present moment, may, according to their composition and their chemical deportment, be arranged in two different classes. If the composition of amido-compounds be expressed by the general formula $C_xH_{(y-2)}(NH_3)''O_z$*) the difference in the mode of formation of the two classes may be illustrated by the following equations:—

I. $2[C_xH_{(y-2)}(NH_3)''O_z] + NHO_2 = C_{2x}H_{2(y-2)}(NH_3)''(N_2)''O_{2z} + 2H_2O.$
II. $C_xH_{(y-2)}(NH_3)''O_z + NHO_2 = C_xH_{(y-2)}(N_2)''O_z + 2H_2O.$

Whilst thus in the first case the substitution of three atoms of hydrogen by one atom of nitrogen takes place in two atoms of the amido-compound, it is in the second case confined to one atom.

Hence it is obvious that for every amido-compound there must be two corresponding nitrogen-substituted bodies.

The conditions which have to be observed in order to lead the reaction, at will, either in the one direction or the other, differ occasionally according to the special character of the amido-compound; but in general it may be taken as a rule that the action of nitrous acid upon neutral solutions of the amido-compounds gives rise to compounds of the first class, whilst those obtained by employing an acid solution belong to the second class.

I have up to the present moment chiefly submitted to minute

* Chemists are not agreed upon the rational constitution of amido-compounds. They are frequently referred to the ammonia-type, and almost as frequently to the same type to which the nitro-compounds from which they are derived belong. In the latter case the group NH_2 is considered as replacing one atom, or NH_3 as taking the place of two atoms of hydrogen. Aniline can thus be written in three different ways, and expressed by the three formulæ,

$\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N,$	$C_6H_5(H_2N)',$	$C_6H_4(H_3N)''.$
Phenylamine.	Amidobenzol.	Ammoniabenzol.

The two latter formulæ appear to me to be capable of explaining in the most natural manner the formation of bodies in which nitrogen is substituted for hydrogen.

examination, members of the first series of compounds, for instance, diazo-amidobenzoic acid and diazo-amidobenzol; the latter substance, in order to give a practical illustration, being formed according to the following equation:—

$$2C_6H_7N + NHO_2 = C_{12}H_{11}N_3 + 2H_2O.$$

As a representative of the second class, may be taken diazo-dinitrobenzol, the formation of which takes place thus:—

$$C_6H_3(NO_2)_2NH_2O + NHO_2 = C_6H_2(NO_2)_2N_2O + 2H_2O.$$

To this last group belong also a number of compounds formed from organic bases, the existence of which up to the present time I have communicated only in short notes, as, for instance, diazobenzol ($C_6H_4N_2$), diazonaphthol, &c. I have now had the opportunity of submitting these bodies also to a more minute examination, and I will endeavour to communicate the results which I have obtained in this and several following papers. Here, already, I will mention that all these bodies are particularly distinguished by the great variety of their forms of combination, and that, in this respect, they exhibit peculiarities not to be found elsewhere in the domain of organic chemistry. In the free state they are remarkable for their extraordinary instability, whilst in their combinations, on the other hand, they are comparatively stable. The following examinations were conducted therefore chiefly with the latter. Very conspicuous also are the physical properties of these peculiar substances, as well as the great number of their products of decomposition; in consideration of all these properties, they may be viewed as one of the most interesting classes of chemical compounds.

I have avoided as much as possible discussing their rational constitution, and have abstained from theoretical speculation. I maintain, however, that the two atoms (or the molecule) of nitrogen, N_2, they contain must be considered as equivalent to two atoms of hydrogen, as is the case with the bodies described in my preceding papers, and it is in accordance with this view that the names of the new compounds have been framed.

In the present paper I intend to confine myself solely to the description of diazobenzol and its derivatives.

Nitrate of diazobenzol is of special importance, as the starting point for the preparation of all the other derivatives, and I will, therefore, give its description the precedence.

Nitrate of Diazobenzol, $C_6H_4N_2.NHO_3$.

This substance can be prepared in various ways; most readily, however, by acting with nitrous acid upon a solution of nitrate of aniline. This salt of aniline is not very soluble in cold water; therefore, in order to obtain a concentrated solution of the new compound, it is best to make a thick paste by grinding up a portion of the nitrate with water and submitting it to the action of the gas, when the undissolved portion of the aniline-salt rapidly disappears, and the whole is converted into the new body. The reaction being accompanied by considerable increase of temperature, it is necessary to keep the solution cool, and to guard against passing a too-rapid current of the gas. The temperature of the solution should not rise much above 30° C. The operation is interrupted as soon as the whole of the aniline has disappeared. This can be ascertained by adding a little strong solution of potassa to a portion of the liquid on a watch-glass, when, if no more aniline is liberated, it may safely be inferred that the reaction is complete. The nitrate of diazobenzol is almost insoluble in ether, and even in ether mixed with much dilute alcohol, in consequence of which it may readily be obtained in a crystalline state thus:—the solution is first filtered, to remove traces of a brown resin, then mixed with about three times its volume of strong alcohol, and ether added until the precipitation is complete. The crystals are allowed to subside, and then filtered from the mother-liquor. The small quantity of the new body which remains in the mother-liquor may be neglected altogether, as its recovery is accompanied with great difficulty. To remove the last traces of colouring matter, the crystals are taken up with cold dilute alcohol and re-precipitated by the addition of ether, when they are obtained as long white needles.

Analysis, as will be shown further, proves that the new compound has the formula $C_6H_4N_2.NHO_3$. Its formation may be explained by the following equation:—

$$\underset{\text{Nitrate of aniline.}}{C_6H_7N.NHO_3} + \underset{\text{Nitrous acid.}}{NHO_2} = \underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2.NHO_3} + \underset{\text{Water.}}{2H_2O}.$$

Another method of preparing nitrate of diazobenzol is based upon the action of nitrous acid upon diazo-amidobenzol, a body

described in a previous communication. On dissolving this latter compound in cold ether, and passing a current of nitrous acid gas through the solution, long acicular crystals of the new substance soon appear. The action should be continued as long as crystals form. The compound so obtained is collected on a filter and washed with ether. The reaction is expressed by the following equation :—

$$\underset{\text{Diazo-amido-benzol.}}{C_{12}H_{11}N_3} + NHO_2 + 2NHO_3 = 2(\underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2.NHO_3}) + 2H_2O.$$

However elegant and simple this method of preparation of the nitrate of diazobenzol may appear, it will scarcely ever be employed, since it involves the previous preparation of diazo-amidobenzol, a body which it is rather troublesome to obtain in large quantities. Nitrate of diazobenzol can also be procured by the direct action of nitrous acid upon a mixture of aniline with about four times its volume of alcohol. The gas is passed into the alcoholic solution till, on the addition of ether to a small portion of it, a copious precipitation of white acicular crystals is produced. When this point is reached, the whole of the reddish-brown solution is mixed with ether, and the precipitate purified as already described.

This method of preparing the nitrate, however, is not suitable when large quantities have to be prepared. It is similar in principle to the preparation by means of diazo-amidobenzol, since to all appearance the aniline is first converted into this compound.

The methods just described, although simple, will only give favourable results when strict attention is paid to the directions given above; for it happens sometimes, and especially when the temperature of the solution is allowed to rise too high, that a copious evolution of nitrogen gas ensues, which cannot be stopped by any means before the whole of the substance has been destroyed.

By employing the first of the above processes, it is sometimes found that, on the addition of ether to the weak alcoholic solution of the crude compound, no crystals separate, but that an aqueous layer is deposited at the bottom of the vessel. This, however, happens only when an insufficient amount of alcohol has been originally added to the solution, because in this case the ether, not being able to mix with the liquor, causes no separation of

crystals to take place. If this occurs, it is best to remove the ethereal liquor, and dilute the residuary aqueous solution with strong alcohol, when, on the addition of ether, crystallisation invariably ensues.

The nitrate of diazobenzol, by whatever method it may have been prepared, crystallises in long white needles, which have been obtained several inches long, and are very soluble in water, less so in alcohol, and almost insoluble in ether and benzol. They can be dried over sulphuric acid without undergoing any change. Heated even below 100° C., they explode with unparallelled violence, far surpassing that of fulminating mercury or iodide of nitrogen. About a gramme of this substance causes by its explosion a concussion like that produced by firing a pistol.

The destructive action of such an explosion is likewise extreme. Iron slabs of several lines in thickness were found smashed to atoms when a somewhat larger quantity was exploded upon them. Friction, pressure, and concussion also cause it to explode. The smallest particles of this substance, accidentally dropped upon the floor of a room, when trodden upon when dry, gave rise to a series of explosions attended with flashes of light. The properties of the nitrate of diazobenzol render it absolutely necessary that the greatest precaution should be observed when manipulating it. The portion of the substance required for analysis having been well washed with ether,* was placed in a platinum crucible and dried over sulphuric acid. Concussion or pressure had to be carefully avoided, especially with the dry substance, on account of its great explosiveness.

* When it is intended to recover the ether employed in the preparation of nitrate of diazobenzol, it is advisable, in order to avoid explosions, to shake the ethereal mother-liquor first with a little water, so as to dissolve any traces of the diazo-compound suspended in it. I have had a most dangerous explosion by neglecting this simple precaution. A large quantity of ether, which had been employed for the precipitation of the new compound from its alcoholic solution, had accumulated. From this liquid a few crystals were observed to have separated. Their number seemed, however, to be so small that it was deemed unnecessary to remove them from the vessel containing the ethereal liquid for distillation. As soon as the vessel became warm in the water-bath, and before the boiling-point of the ether had been reached, a fearful explosion took place, shattering the whole of the distilling apparatus to pieces, and setting fire to the ether, the flame of which spread most alarmingly through the laboratory. The gas-flames, which were burning at the time in the room, were suddenly extinguished by the violent pressure upon the atmosphere, and all those working in the laboratory (who fortunately escaped unhurt) were for a moment deprived of their breath. The explosive properties of the nitrate of diazobenzol may perhaps at a future period find practical application.

For the above mentioned reasons I abstained from analyzing this compound in the usual manner, especially as I had opportunities of ascertaining the composition of analogous but less dangerous compounds by the ordinary analytical methods. I have, however, been enabled to arrive at a knowledge of the composition of nitrate of diazobenzol by the very interesting change which an aqueous solution undergoes by the action of heat. By ebullition the compound is transformed under the influence of the water into carbolic acid, nitrogen, and nitric acid; and by estimating the quantities of the two latter products I have arrived at the true composition of the explosive substance:

$$\underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2.NHO_3} + H_2O = \underset{\text{Carbolic acid.}}{C_6H_6O} + NHO_3 + N_2.$$

The method employed for the determination of the quantity of nitrogen evolved by the ebullition of the aqueous solution of the explosive compound is as follows:—The solution was introduced into a flask and a stream of carbonic acid gas passed through it. When the air was expelled, the delivery-tube was placed under a graduated cylinder containing solution of potassa, and the contents of the flask heated to ebullition.*

I. 0·605 grm. of the compound, treated as above, gave 80·4 cub. centims. of nitrogen at 0°, and 760 millims. bar. pressure = 0·101 grm. of nitrogen, or 16·70 per cent.

	Theory.	Experiment.
N =	17·77	16·70

II. ·492 grm. of substance, dissolved in water and boiled, required for neutralisation 29·5 cub. centims. of $\frac{1}{10}$ standard alkali solution, corresponding to 0·185 grm. of nitric acid, or 37·77 per cent.

	Calculated.		Found.
$C_6H_4N_2$ ..	190	62·27	——
NHO_3....	63	37·73	37·77
	253	100·00	

Sulphate of Diazobenzol, $C_6H_4N_2.SH_2O_4$.

Acid sulphate of aniline, when treated with nitrous acid, is

* In all analyses mentioned herein the analyzed substances are understood to be desiccated by sulphuric acid previously, unless the contrary is distinctly stated.

converted into sulphate of diazobenzol according to the equation—

$$*C_6H_7N.\overset{\uparrow}{S}H_2O_4 + NHO_2 = C_7H_4N_2.\overset{\uparrow}{S}H_2O_4 + 2H_2O.$$

Acid sulphate of aniline. Sulphate of diazobenzol.

On account of the slight solubility of sulphate of aniline, and in order to avoid employing a large quantity of liquid, it becomes necessary to suspend the salt in water, and to expose it in this state to the action of nitrous acid. The reaction, however, is very slow, and the salt is only gradually converted into the diazo-compound. I found it, therefore, more convenient to prepare the sulphate from the nitrate of diazobenzol, by treating a concentrated aqueous solution† of the latter with a sufficient quantity of sulphuric acid, previously diluted to avoid rise of temperature upon addition.

The solution thus obtained is then mixed with three times its volume of absolute alcohol, and lastly, with a sufficient amount of ether, which causes the sulphate of diazobenzol, together with some water, to separate in a layer at the bottom of the vessel, the liberated nitric acid, together with the excess of sulphuric acid, remaining mixed with the supernatant alcohol and ether. This latter is decanted, and the solution of the sulphate (with a view to the removal of a further quantity of water) is once more treated with absolute alcohol and reprecipitated by means of ether. The precipitated liquid is then placed in flat dishes over sulphuric acid, when it soon solidifies to a magma of white crystals. In order to purify these crystals completely, they are washed on a filter with a mixture of alcohol and ether, which removes any trace of sulphuric and carbolic acids that may have been produced by a partial decomposition of the sulphate of diazobenzol, then dissolved in weak cold alcohol, and precipitated by the addition of ether. The crystals are separated without delay from the mother-liquor and dried over sulphuric acid.

Sulphate of diazobenzol crystallises in prisms, which readily dissolve in water, but are soluble with difficulty in absolute alcohol and insoluble in ether. The aqueous, as well as the alcoholic,

* Ordinary sulphate of aniline containing excess of free sulphuric acid is understood by this formula.

† The crude solution obtained by the action of nitrous acid upon nitrate of aniline may be employed.

solution is decomposed on boiling with evolution of gas. Exposed to the air, this compound attracts moisture very rapidly, becomes liquid, and gradually decomposes. Heated alone, it deflagrates feebly at about 100° C.

Hydrobromate of Diazobenzol, $C_6H_4N_2$,HBr.

This compound is prepared by the action of bromine upon diazo-amidobenzol. When an ethereal solution of bromine is gradually added to a rather concentrated solution of the diazo-amido-compound, each drop of the bromine-solution is seen to produce a precipitation of the hydrobromate of diazobenzol. When no more crystals are formed, the precipitate is separated from the mother-liquor, washed with ether till quite white, and then dried over sulphuric acid. All these operations must be performed as speedily as possible, since the new compound is of a very unstable nature and rapidly decomposes.

Should it be found necessary to recrystallise the precipitate, it must be dissolved in the least possible quantity of cold alcohol, and ether added to the solution till no more precipitation takes place.

Hydrobromate of diazobenzol crystallises in white nacreous scales, which, like the compound previously described, are readily soluble in water, less so in alcohol, and insoluble in ether. The solution of this compound is distinguished by a strong acid reaction. Heat, friction, and pressure cause the crystals of the hydrobromate to explode with the same violence as the nitrate of diazobenzol. Even when in a perfectly dry state, this compound can only be kept for a short time without undergoing decomposition (which is accompanied by the production of a peculiar aromatic odour), the decomposition being complete in a few days. It is formed according to the equation,

$$\underset{\text{Diazo-amido-benzol.}}{C_{12}H_{11}N_2} + 6Br = \underset{\text{Hydrobromate of diazobenzol.}}{C_6H_4N_2.HBr} + \underset{\text{Tribromaniline.}}{C_6H_4Br_3N} + 2HBr.$$

Tribromaniline remains in the ethereal mother-liquor, from which it crystallises on evaporation.

It is most likely that, by the action of chlorine upon diazo-amidobenzol, hydrochlorate of diazobenzol may be obtained. An aqueous solution of this latter compound, however, may also be

prepared by treating a solution of the hydrobromate with moist chloride of silver.

Perbromide of Diazobenzol, $C_6H_4N_2,HBr.Br_2$.

On adding a small quantity of bromine-water to an aqueous solution of the nitrate of diazobenzol, a white crystalline precipitate of tribromophenylic acid is usually obtained, owing to the presence of a small quantity of phenylic acid formed by the spontaneous decomposition of the nitrate by water. On removing the tribromophenylic acid as quickly as possible by filtration, and on adding a large excess of bromine-water containing free hydrobromic acid to the filtrate, the new bromine-compound separates as a brownish-red oil, which solidifies to a crystalline mass soon after the supernatant liquor has been removed. The crystals are obtained pure for analysis by washing with a little ether.

Perbromide of diazobenzol, which crystallises in yellow plates, is insoluble in water, rather difficultly soluble in alcohol, and insoluble in ether. It is comparatively stable when dry. Its alcoholic solution, on the other hand, rapidly decomposes, even in the cold, with evolution of gas. For this reason it is impossible to recrystallise it without loss. In order to purify this unstable perbromide, it is most advantageous to dissolve it in cold alcohol, and to allow the solvent to evaporate spontaneously in shallow vessels in the open air. Very fine crystals are usually obtained in this manner, but contaminated with trifling quantities of an oily product of decomposition, which, however, may be removed by washing with a little cold ether. On application of heat this compound deflagrates at a comparatively low temperature. The constitution of the perbromide of diazobenzol appears to be the same as that of periodide of tetrethylammonium and similar compounds of other bases.

Platinum-salt of Hydrochlorate of Diazobenzol, $C_6H_4N_2.HCl.PtCl_2$,

is obtained by the addition of bichloride of platinum to a rather concentrated aqueous solution of the nitrate of diazobenzol. The fine yellow prisms which are precipitated are almost insoluble in alcohol and ether. They are rather stable; when kept for some time, however, they acquire a brownish colour, and are gradually

but completely decomposed. On heating they deflagrate; hence it it is impossible to estimate the platinum by simple ignition.

Gold-salt of Hydrochlorate of Diazobenzol, $C_6H_4N_2HCl,AuCl_3$.

By the addition of terchloride of gold to a dilute aqueous solution of the nitrate of diazobenzol, this compound is obtained in the form of a light-yellow crystalline precipitate, insoluble in water, but soluble in alcohol, especially when warm, from which on cooling, it is deposited in the form of small golden-yellow plates. This salt cannot, however, be recrystallized without some loss, especially when the alcoholic solution is heated to boiling. The decomposition is indicated invariably by an evolution of gas; continued boiling with alcohol destroys it completely.

It is well known that when bromine, chlorine, or hyponitric acid is substituted in organic compounds for certain hydrogen atoms, the product formed is distinguished from the original compound, if the latter be an acid, by stronger acid properties, or if a base, by less pronounced basic characters; and also that the contrary is observed in the case of substitution of potassium, NH_2, &c., for the same hydrogen-atoms.

Nitrogen, however, exhibits in this respect a peculiar double nature, since it is found only slightly (or not at all) to affect the basic properties of a compound, whilst at the same time it exerts so decided an acidulating action as to impart to strong bases an acid nature. I have already clearly shown that diazobenzol has all the characters of an organic base, capable, like aniline, of forming saline compounds with acids. It possesses, at the same time, the property of combining with metallic hydrates, playing, to a certain extent, the part of an acid. These metallic derivatives are, as a rule, distinguished by the same instability as the compounds of diazobenzol with acids. They are less affected, however, by heat. Their aqueous or alcoholic solutions can be heated to boiling for some time without suffering complete decomposition. Heated alone they explode, although at a much higher temperature, and not with so great violence as the bodies previously described. The compounds which are soluble in water are mostly well crystallised, whilst the insoluble ones, such as those formed with silver and lead, are obtained as amorphous precipitates.

Compound of Hydrate of Potassium with Diazobenzol, $C_6H_4N_2.KHO$.

By introducing a very concentrated solution of nitrate of diazobenzol into an excess of an equally concentrated solution of caustic potash, drop by drop, a yellowish liquid is obtained possessing a peculiar aromatic odour, and solidifying, by evaporation in the water-bath, to a crystalline mass. This is a mixture of the compound of hydrate of potassium with diazobenzol and nitre, together with a brownish-red amorphous body—the result of a secondary reaction which a portion of the original substance undergoes, and which is always indicated by the evolution of gas. In order to separate these bodies it is necessary to remove the excess of caustic potash. This is best done by putting the crystalline mass into a strong linen cloth and squeezing it powerfully between porous stones. The dry cake is then treated with absolute alcohol, which readily dissolves the compound of hydrate of potassium with diazobenzol, leaving the nitrate of potassium insoluble; it is then separated by filtration. The alcoholic filtrate (which, on account of the above-mentioned secondary product of decomposition, possesses an intense reddish-brown colour) is then evaporated on the water-bath. The residue is once more pressed and washed with a mixture of alcohol and ether to remove the reddish-brown substance; the compound is then obtained nearly white. By again pressing and dissolving the dry cake in a small quantity of absolute alcohol, filtering, and adding a sufficient amount of ether, the substance is obtained in white plates, which must be dried at once over sulphuric acid.

The compound of hydrate of potassium with diazobenzol crystallises in small, white, soft plates, which become reddish by exposure to the air; they are very readily soluble in water and alcohol, but insoluble in ether. The solution has a strong alkaline reaction. A freshly prepared aqueous solution is but slightly coloured; but by keeping for a short time, it rapidly acquires a yellow colour, and ultimately a reddish-yellow substance is precipitated. Ebullition does not seem to accelerate this decomposition materially. The dry substance is very stable, and can be kept a long time unchanged. Heated alone it explodes at a little above 130°; the explosion is accompanied by a slight report.

Compound of Hydrate of Silver with Diazobenzol, $C_6H_4N_2.AgHO$.

This is obtained as a white or slightly chocolate-coloured precipitate, by treating a freshly prepared solution of the previous compound with a solution of nitrate of silver. After removing the mother-liquor, the precipitate is thoroughly washed with water, dried by pressing between filter-paper, and finally over sulphuric acid.

The compound of hydrate of silver with diazobenzol is insoluble in all the ordinary neutral solvents. Nitric acid even when cold dissolves it with great facility. It is distinguished by great stability; for even after having been kept for weeks, not the least sign of decomposition could be discovered. Exposed to a higher temperature it explodes with some violence.

Compound of Hydrate of Barium with Diazobenzol.

This compound is obtained when a solution of a very soluble barium-salt is added to a rather concentrated solution of the potassium-compound. It is precipitated in the form of white, microscopic, indistinct needles or plates, which become yellowish in consequence of a gradual decomposition. It is difficultly soluble in water.

The compound of diazobenzol with hydrate of zinc is a white amorphous powder insoluble in water. The compound with hydrate of lead is also a white powder, but acquiring rapidly a yellow colour. With sulphate of copper a brown precipitate changing to green is obtained. Mercuric chloride gives a white precipitate.

Diazobenzol, $C_6H_4N_2$.

This remarkable substance is obtained when an aqueous solution of the compound of hydrate of potassium with diazobenzol is treated with a sufficient quantity of acetic acid. A thick yellow oil it liberated, which possesses a peculiar odour, and is remarkable for its extraordinary instability. Its existence is very ephemeral, and after a short time nitrogen gas begins to be evolved, and the oil is rapidly converted into a brownish-red substance. The heat which is produced when larger quantities of the oil undergo this spontaneous decomposition is sufficient to give rise to dangerous explosions.

The addition of ether to the oil dissolves it instantaneously, producing a red solution, a tumultuous evolution of gas taking place. It combines with nitric and sulphuric acids, and with hydrate of potassa, terchloride of gold, &c., forming the compounds previously described.

Compounds of Diazobenzol with Organic Bases.

Diazo-amidobenzol, as is well known, is formed by the action of nitrous acid upon an alcoholic solution of aniline, according to the equation

$$\underset{\text{Aniline.}}{2C_6H_7N} + NHO_2 = \underset{\text{Diazo-amidobenzol.}}{C_{12}H_{11}N_3} + 2H_2O.$$

By viewing this body as a double compound of diazobenzol and aniline,

$$C_{12}H_{11}N_3 = \begin{cases} C_6H_4N_2, \\ C_6H_7N, \end{cases}$$

I was led to prepare it by the direct action of aniline upon compounds of diazobenzol. This reaction proceeds readily on mixing an aqueous solution of nitrate of diazobenzol with aniline, when a viscid yellow mass is speedily produced, which becomes crystalline after a short time, and can be obtained in a perfectly pure state by several recrystallisations* from alcohol. The formation of the diazo-amidobenzol may be expressed as follows :—

$$\underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2.NHO_3} + \underset{\text{Aniline.}}{2C_6H_7N} = \underset{\text{Diazo-amidobenzol.}}{C_{12}H_{11}N_3} + \underset{\text{Nitrate of aniline.}}{C_6H_7N.NHO_3}.$$

On referring to the equation given on page 39 for the formation of nitrate of diazobenzol from diazo-amidobenzol,

$$C_{12}H_{11}N_3 + NHO_2 + 2NHO_3 = 2(C_6H_4N_2.NHO_3) + 2H_2O,$$

it is seen that these two bodies may be readily transformed into one another.

Many other bases deport themselves with nitrate of diazobenzol exactly like aniline, and we may therefore look forward to the dis-

* Any excess of aniline must be removed by means of acetic acid before crystallisation.

covery of a large number of double compounds analogous to diazo-amidobenzol.

It is not my intention to give a full history of these compounds, as a few short statements will show clearly how closely they are allied to their prototype diazo-amidobenzol.

Diazobenzol-amidobromobenzol, $\left\{\begin{matrix}C_6H_4N_2\\C_6H_6BrN\end{matrix}\right\}$.

This compound is obtained by the action of bromaniline upon nitrate of diazobenzol. It crystallises in very fine small yellow plates or needles, which are rather difficultly soluble in alcohol, but readily soluble in ether. Its platinum-salt,

$$C_{12}H_{10}BrN_3.H_2Cl_2.2PtCl_2,$$

is obtained as a buff-coloured precipitate consisting of fine hair-like crystals. Nitrate of silver produces, in an alcoholic solution, a yellow precipitate similar to that of the compound previously described.

In the formation of the above bodies, two atoms of base enter into chemical action with one atom of nitrate of diazobenzol, forming, together with the diazo-amido-compound, the nitrate of the base employed. Naphtalidine (amidonaphtol), however, combines directly in equal numbers of atoms with nitrate of diazobenzol, giving rise to a compound which has the formula

$$C_{16}H_{14}N_4O_3,$$

and which, as will be shown, must be viewed as nitrate of diazobenzol-amidonaphtol: $=\left\{\begin{matrix}C_6H_4N_2\\C_{10}H_9N\end{matrix}\right\}NHO_3$. This compound is obtained in an impure state as a violet crystalline precipitate on adding an aqueous solution of nitrate of diazobenzol to an alcoholic solution of naphtalidine. It is purified by repeated washings with cold alcohol and recrystallisation from the same, forming beautiful green prisms.

Its formation takes place according to the equation

$$\underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2NHO_3} + \underset{\text{Naphtalidine.}}{C_{10}H_9N} = \underset{\text{Nitrate of diazobenzol-amidonaphtol.}}{C_{16}H_{14}N_4O_3}.$$

It is one of the finest bodies of which chemistry can boast. It crystallises in well-defined prisms, which by reflected light are of a magnificent grass-green colour, but ruby-red by transmitted light. The crystals are almost insoluble in water and ether. Hot alcohol dissolves them freely, and redeposits them almost entirely on cooling.

Diazobenzol-amidonaphtol, $\left.\begin{matrix} C_6H_4N_2 \\ C_{10}H_9N \end{matrix}\right\}$.

This compound is obtained from the previous substance by removing the nitric acid by means of ammonia or potassa. It crystallises in very brilliant ruby-red prisms, readily soluble in alcohol and ether, forming yellow liquids. Acids impart a beautiful violet colour to these solutions. Bichloride of platinum produces a purple-blue crystalline precipitate; nitrate of silver a yellow precipitate, which consists of small fine needles.

It is worth mentioning that these diazobenzol-amido-compounds can also be obtained by acting with an aqueous solution of the salts of the respective bases upon the compound of hydrate of potassium with diazobenzol. The reaction which takes place may be expressed by the following equation :—

$$\underset{\text{Hydrate of potassium with diazobenzol.}}{C_6H_4N_2KHO} + \underset{\text{Hydrochlorate of aniline.}}{C_6H_7NHCl} = \underset{\text{Diazo-amido-benzol.}}{C_{12}H_{11}N_3} + KCl + H_2O.$$

Compounds of Diazobenzol with Amido-Acids.

Amido-acids are likewise capable of entering into combination with diazobenzol. One would have expected that the compounds to which this reaction gives rise would deport themselves in an analogous manner to the sulphate or nitrate of diazobenzol, which, like the salts of organic bases, are capable of double decomposition. This, however, is not the case. The compounds of diazobenzol with amido-acids behave more like simple bodies, exhibiting much similarity to the diazo-amidobenzol, being capable, like the latter, of forming, with bichloride of platinum, double compounds of the nature of the potassio-bichloride of platinum. They possess, moreover, the property of combining with metals, giving rise to bodies which correspond entirely to the salts of simple acids.

Diazobenzol-amidobenzoic acid, $\left\{\begin{matrix} C_6H_4N_2 \\ C_7H_7NO_2 \end{matrix}\right.$.

This compound is obtained by simply mixing an aqueous solution of the nitrate of diazobenzol (1 molecule) with a solution of amidobenzoic acid (2 molecules). It separates as a yellow crystalline precipitate which is readily freed from the mother-liquor, and when dry dissolved in ether and filtered. The ethereal solution deposits on evaporation yellow crystals, which are obtained pure for analysis by washing with cold alcohol.

This body is formed according to the equation

$$C_6H_4N_2.NHO_3 + 2C_7H_7NO_2 = C_{13}H_{11}N_3O_2 + C_7H_7NO_2.NHO_3.$$

Nitrate of diazobenzol. — Amidobenzoic acid. — Diazobenzol-amidobenzoic acid. — Nitrate of amidobenzoic acid.

Diazobenzol-amidobenzoic acid forms small indistinct plates or crystalline grains. It is almost insoluble in water, very difficultly soluble in alcohol, and easily soluble in ether. Solutions of ammonia, potash, or carbonate of potassium dissolve the acid readily, the solution acquiring a yellow colour. On heating a little of the substance on platinum-foil, it fuses, and is rapidly decomposed, the decomposition being accompanied by a violent evolution of gas.

Cold dilute mineral acids act upon it but slowly; on heating, however, speedy decomposition ensues. Acetic acid, even when highly concentrated, has no action in the cold, but on the application of heat destroys it.

Platinum-salt of the Hydrochlorate of Diazobenzol-amidobenzoic Acid, $C_{13}H_{11}N_3O_2.2HCl.2PtCl_2$.

This compound forms small yellowish-white indistinct plates, and is obtained by adding an alcoholic solution of bichloride of platinum to the ethereal solution of the diazobenzol-amidobenzoic acid.

Diazobenzol-amidobenzoic acid in its behaviour with bases is similar to a bibasic acid, since it combines with metallic bodies in two ways. All the salts formed are comparatively stable; those, for example, which are soluble in water, as the potassium-salt, will even bear recrystallisation. With the oxide of silver and barium it

forms insoluble precipitates. A more minute description of these compounds I must defer to a future time.

Compounds analogous to diazobenzol-amidobenzoic acid are formed when amido-dracylic acid (isoamidobenzoic acid), amido-anisic acid, &c. are made to react in the manner previously described upon nitrate of diazobenzol. It is my intention to investigate these compounds more specially, and I therefore abstain from entering further upon their description, only noticing that they possess a remarkable resemblance to diazobenzol-amidobenzoic acid.

Imidogen Compounds of Diazobenzol.

By this name are designated a peculiar class of diazobenzol-compounds obtained by the action of ammonia, ethylamine, and analogous organic bases upon perbromide of diazobenzol ($C_4H_4N_2$. $HBr.Br_2$). All the compounds hitherto described exist in the solid state, and none of them can be volatilised without decomposition; the new compounds to be described, on the other hand, are liquids which can be distilled, and which possess the narcotic odour of some vegetable bases, such as conidine and nicotine. Beyond this odour, however, they have nothing in common with these natural bases. They are indifferent bodies, combining with neither acids nor bases.

Diazobenzolimide, $C_6H_5N_3 = \left.\begin{matrix}(C_6H_4N_2)'' \\ H\end{matrix}\right\}N.$

On treating perbromide of diazobenzol with aqueous ammonia, a speedy decomposition ensues with evolution of much heat. The products of the reaction are, first, bromide of ammonium, which passes into solution; secondly, diazobenzolimide, which separates as a heavy oil, rather highly coloured by a brown substance simultaneously produced in small quantity. By repeatedly distilling the oil with water it is obtained perfectly pure, and of a slightly yellowish colour; the substance which imparts to it the intense brownish colour not being volatile, is left behind in the retort. The purified oil is separated from the water by a separating funnel, placed over chloride of calcium, and then distilled once more from a water-bath *in vacuo*.

Its formation is explained by the following equation:—

$$\underset{\text{Perbromide.}}{C_6H_4N_2.HBr.Br_2} + 4NH_3 = \left.\begin{matrix}C_6H_4N_2\\H\end{matrix}\right\}N + 3NH_4Br.$$
Diazobenzolimide.

Diazobenzolimide is remarkable for its narcotic, aromatic-ammoniacal odour. It is volatilised by distillation with water, and also when heated *in vacuo*, as shown above. When distilled at the ordinary atmospheric pressure, it decomposes with explosive violence. Alcohol and ether dissolve it with some difficulty. I could not succeed in solidifying the oil by using a frigorific mixture of nitre and sal-ammoniac. Hydrochloric acid, even when concentrated, and aqueous potassa have no effect upon it. Strong nitric and sulphuric acids dissolve it with decomposition.

$$\textit{Ethyldiazobenzolimine} = \left.\begin{matrix}(C_6H_4N_2)''\\C_2H_5\end{matrix}\right\}N.$$

This body is obtained in a manner exactly similar to the one employed for the preparation of diazobenzolimide, viz., by acting with ethylamine upon the perbromide of diazobenzol. It is likewise a yellowish-coloured oil, having a deceptive resemblance to the previously described compound.

Products of Decomposition of the Diazobenzol-compounds.

The transformations which the molecule of diazobenzol undergoes through the influence of various reagents are numerous, and there is probably no other body to be met with in the large field of organic chemistry that surpasses it in this respect. The products of decomposition to which it gives rise frequently possess new and very distinctive features; more frequently, however, they belong to the benzol or phenyl group, in which latter case their formation depends upon the great inclination which the two nitrogen-atoms of the diazobenzol exhibit to escape and to cede their place to other atomic groups of the same value (HH).

Deportment of Diazobenzol-compounds when boiled in an aqueous solution.

The transformation of nitrate of diazobenzol, under the influence of boiling water, has already been noticed. A similar

change is observed with regard to its sulphate and hydrobromate, as will be seen from the following equations:—

$$\underset{\text{Sulphate of diazobenzol.}}{C_6H_4N_2.SH_2O_4} + H_2O = \underset{\text{Phenylic acid.}}{C_6H_6O} + SH_2O_4 + N_2.$$

$$\underset{\text{Hydrobromate of diazobenzol.}}{C_6H_4N_2.HBr} + H_2O = \underset{\text{Phenylic acid.}}{C_6H_6O} + HBr + N_2.$$

On the other hand, the compounds of diazobenzol with metallic hydrates exhibit a very different deportment with boiling water. By neutralizing the metal, however, with a mineral acid, the decomposition takes place in accordance with the above equations.

Action of Alcohol upon Nitrate of Diazobenzol.

By gradually and cautiously introducing the nitrate of diazobenzol into a moderate quantity of alcohol (previously warmed to about 50° C. in order to accelerate the solution), and submitting the whole to distillation in a water-bath, a yellow residue remains, which solidifies to a crystalline mass on cooling, and dissolves readily in alkaline solutions, whence it was inferred that it had the character of an acid. There was, in fact, no difficulty in ascertaining that this body was nothing else than dinitrophenylic acid, possessing all the well-pronounced properties of this compound; and to prove this most conclusively, it was converted into the characteristic amidonitrophenylic acid. Dinitrophenylic acid, however, is not the only product to which this reaction gives rise; for on mixing the distillate with water, an oily body separates, which collects upon the liquid, especially when its specific gravity has been increased by the addition of a solution of chloride of sodium. This oil may be removed by means of a separating funnel and dried over chloride of calcium. It possesses, when rectified by distillation, all the properties of ordinary benzol. I have converted it into dinitrobenzol by the action of fuming nitric acid, and have found this latter identical with that prepared from coal-tarbenzol. The fusing-point of the dinitrobenzol was in both instances 89° C. The production of dinitrocarbolic acid and of benzol can be expressed by the following equation:—

$$\underset{\text{Nitrate of diazobenzol.}}{2(C_6H_4N_2NHO_3)} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Dinitrophenylic acid.}}{C_6H_4(NO_2)_2O} + \underset{\text{Benzol.}}{C_6H_6} + \underset{\text{Aldehyde.}}{C_2H_4O} + N_4 + H_2O.$$

Sulphate of diazobenzol, when distilled with alcohol, is acted upon in a similar manner. The alcoholic distillate contains the benzol, whilst the residue in the flask consists of sulphuric acid and a small quantity of an organic acid.

Deportment of Nitric Acid and Nitrate of Diazobenzol.

Ordinary nitric acid, as well as the fuming acid, has no action upon this compound in the cold. The diazo-compound was dissolved in the strongest fuming nitric acid, allowed to stand for one hour, and cautiously diluted with water so as to prevent any rise of temperature; solution of terchloride of gold was then added, which gave an immediate precipitate. Analysis showed this precipitate to be identical with the gold-salt of hydrochlorate of diazobenzol.

On boiling the solution of nitrate of diazobenzol in fuming nitric acid, trinitrophenylic acid is produced. By employing a somewhat weaker acid, an admixture of tri- and di-nitrophenylic acid is obtained.

Action of Sulphuric Acid upon Sulphate of Diazobenzol.

On dissolving the sulphate in a small quantity of concentrated sulphuric acid, and heating in a water-bath, a copious evolution of nitrogen gas ensues, and a brownish-coloured liquid remains, consisting of a mixture of the excess of acid employed and a new sulpho-acid. The separation of the two acids is readily accomplished by preparing their barium-salts. After diluting the brownish liquid with a sufficient quantity of water, and adding carbonate of barium as long as the solution exhibits an acid reaction, the insoluble sulphate of barium may be separated by filtration from the barium-salt of the new sulpho-acid. The filtrate is evaporated till a pellicle forms, when, on cooling, a large quantity of crystals of the barium-salt of the new sulpho-acid appears. After separating the crystals by filtration, and then evaporating the mother-liquor further and cooling, a new quantity of crystals is obtained. A single recrystallisation from water renders them perfectly pure. This salt forms fine, white, well-developed prisms, attaining frequently to the length of half an inch, when the solution is allowed to cool very slowly. The crystals are readily soluble in hot, rather difficultly in cold water, and almost insoluble

in alcohol and ether. The solutions have a neutral reaction. The substance was dried at 160° C.; and on analysis gave numbers which agree with the formula

$$C_6H_6Ba_2S_2O_8.$$

The salt, dried over sulphuric acid, contained $3\frac{1}{2}$ atoms of water of crystallisation, which escaped entirely at 130° C.

In accordance with the analysis of the barium-salt, the free acid must be expressed by the formula $C_6H_8S_2O_8$, and I propose to call it *disulphophenylenic acid*, since it may be viewed as a compound of two molecules of sulphuric acid with the hypothetical hydrocarbon C_6H_4 (phenylene), viz., $C_6H_4S_2H_4O_8$. Its formation may be thus expressed :—

$$\underset{\text{Sulphate of diazobenzol.}}{C_6H_4N_2.SH_2O_4} + SH_2O_4 = \underset{\text{Disulphophenylenic acid.}}{C_6H_4S_2H_4O_8} + N_2.$$

The free acid is easily prepared by dissolving the barium-salt in water, carefully precipitating the barium with sulphuric acid, and concentrating the filtrate on a water-bath till it acquires a syrupy consistency; when placed over sulphuric acid, it crystallises out in the form of warty crystals, which are exceedingly soluble in water and alcohol, and deliquesce in a moist atmosphere.

Besides the compound just described, there exists yet another barium-compound of disulphophenylenic acid of the composition $C_6H_4S_2Ba_3HO_8$, formed by the exchange of a third equivalent of the hydrogen for barium. It is obtained by digesting either the barium-compound with two atoms of barium, or the free disulphophenylenic acid with baryta-water for some time. The excess of baryta is neutralized by carbonic acid, and the filtrate evaporated till it begins to crystallise. The new salt forms very thin white plates, which, on being left for some time in contact with the mother-liquor, are likewise converted into well-formed prisms.

This salt differs, moreover, from the salt containing only two equivalents of barium, by its greater solubility in water,* and the strong alkalinity of its solutions, which is not destroyed by the carbonic acid. When freshly prepared, the crystals of this com-

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pound are clear and transparent; they soon, however, lose a portion of their water of crystallisation, and are reduced to a white powder.

It is possible that two more barium-salts of disulphophenylenic acid exist, having the respective formulæ $C_6H_4S_2BaH_3O_8$ and $C_6H_4S_2Ba_4O_8$.

Disulphophenylenic acid is likewise capable of combining in two proportions with other metals; with lead it seems to combine even more freely, forming apparently no fewer than five distinct salts, viz., $C_6H_4S_2H_3PbO_8$, $C_6H_4S_2H_2Pb_2O_8$, $C_6H_4S_2HPb_3O_8$, $C_6H_4S_2Pb_4O_8$, and $C_6H_4S_2PbO_8.Pb_2O$.

The description of the preparation and properties of these bodies will be reserved for a future communication. The silver-salt of disulphophenylenic acid may, however, find a place here, since it exhibits the peculiar chemical deportment of the new acid in a striking manner.

Disulphophenylenate of Silver is obtained by treating an aqueous solution of the free acid with carbonate of silver, evaporating the filtrate first on the water-bath, and lastly over sulphuric acid. It crystallises either in warty masses or in small plates. It is easily soluble in water, difficultly so in alcohol, and almost insoluble in ether. It does not contain any water of crystallisation. After drying over sulphuric acid it does not lose weight, even when heated to upwards of 160° C.

To judge from the composition of the silver-salt of disulphophenylenic acid, it appears to be bibasic ($C_6H_4S_2H_2O_7$), whilst the formula deduced from its barium and lead salts establishes its tetrabasic character ($C_6H_4S_2H_4O_8$). The new acid exhibits therefore the rare property of varying basicity, such as is possessed by phosphoric acid in the inorganic, and by terebinic acid in organic chemistry, as shown by Ekman.*

Action of Sulphuretted Hydrogen upon the Gold-salt of Hydrochlorate of Diazobenzol.

By passing a current of sulphuretted hydrogen gas through cold water in which the gold-salt has been suspended, all the gold is converted into the trisulphide, whilst the diazobenzol is transformed into a volatile product. When the reaction is complete,

* Limpricht, Lehrbuch der Chemie, p. 1016.

in alcohol and ether. The solutions have a neutral reaction. The substance was dried at 160° C.; and on analysis gave numbers which agree with the formula

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By passing a current of sulphuretted hydrogen gas through cold water in which the gold-salt has been suspended, all the gold is converted into the trisulphide, whilst the diazobenzol is transformed into a volatile product. When the reaction is complete,

* Limpricht, Lehrbuch der Chemie, p. 1016.

the liquid is submitted to distillation, when a very nauseous, heavy, yellowish oil is found to pass over with the aqueous vapour. I have not pursued its examination further than to convince myself that it is not the phenylmercaptan (C_6H_6S) described by Vogt, which at first sight it appeared to be. Its mercaptanic odour and its derivation from the diazobenzol in the gold-compound (according to the equation

$$C_6H_4N_2 + SH_2 = C_6H_6S + N_2)$$

rendered this view very probable. Neither basic acetate of lead, however, nor nitrate of silver, even in presence of ammonia, gave precipitates with the oil, which proved convincingly that it differed entirely from phenylmercaptan.

On examining the residue in the retort after the oil has been distilled off, it was found to consist of tersulphide of gold and an aqueous liquid; the latter is found to contain chloride of ammonium, together with a little free hydrochloric acid, and a small quantity of the hydrochlorate of a base which is no other than aniline. The occurrence of these bodies shows that a small portion of the diazobenzol is decomposed as follows:—

$$C_6H_4N_2 + 3SH_2 = C_6H_7N + NH_3 + 3S.$$

The same products of decomposition are met with when an alcoholic solution of the gold-salt is treated with sulphuretted hydrogen.

On passing the latter, however, over the dry gold-compound, it speedily causes an explosion. By employing only a very small quantity of the substance, and by spreading it in a thin layer in a glass tube, it is possible to avoid explosion and secure a quiet decomposition. The reaction is over when no more hydrochloric acid fumes escape with the current of sulphuretted hydrogen. The black residue which is left behind in the glass tube appears to contain, besides tersulphide of gold, free diazobenzol. I was not able to isolate the latter. The explosive nature of the residue and its deportment with ether, which speedily produces a rapid evolution of gas, leave, however, little doubt of its presence. Hydrochloric acid, tersulphide of gold, and diazobenzol are therefore the products of decomposition of the gold-salt by means of sulphuretted hydrogen.

Action of Nascent Hydrogen upon Diazobenzolimide.

If hydrogen is generated by means of zinc and sulphuric acid in an alcoholic solution of this body, a point is reached in a comparatively short time when, on the addition of water, no more turbidity occurs, indicating that the diazobenzolimide has completely disappeared.

By removing the excess of zinc and evaporating the alcohol on a water-bath, the residue, when treated with potassa, evolves much ammonia—an oily base simultaneously separates; this is purified by distillation, and is found to be identical with ordinary aniline. The decomposition may be thus expressed:—

$$\underset{\text{Diazobenzolimide.}}{C_6H_5N_3} + 8H = \underset{\text{Aniline.}}{C_6H_7N} + 2NH_3.$$

Action of Carbonate of Barium upon Nitrate of Diazobenzol.

By treating a cold aqueous solution of this salt with levigated carbonate of barium, a feeble evolution of gas is observed, which lasts for several days. A reddish-brown mass is produced insoluble in water, which remains with the excess of carbonate of barium when the reaction is over. The residue is a mixture of two distinct bodies. By filtering off the solution containing nitrate of barium and removing the excess of carbonate by means of dilute hydrochloric acid, these two products can be readily separated by treatment with cold alcohol, in which they are very unequally soluble. In order to obtain the more soluble one in a pure state, the alcohol is evaporated and the residue treated with ammonia. An intensely yellow-coloured solution is produced, which must be filtered to remove a small quantity of a resinous substance, and decomposed with hydrochloric acid, when the new compound is precipitated in crystals. These are obtained perfectly pure for analysis by repeated crystallisation from weak alcohol.

The formation of this compound may be expressed by the following equation:—

$$\underset{\text{Nitrate of diazobenzol.}}{2(C_6H_4N_2.NHO_3)} + H_2O = \underset{\text{New compound.}}{C_{12}H_{10}N_2O} + 2NHO_3 + N_2.$$

It will be readily seen that this formula contains the elements of phenylic acid and diazobenzol*

$$C_6H_4N_2 + C_6H_6O = C_{12}H_{10}N_2O.$$

I will, therefore, call it *phenol-diazobenzol* without prejudging its rational constitution. This body usually crystallises from alcohol and ether (in which it is very easily soluble) in brittle brownish-yellow warts. It is almost insoluble in cold water, slightly so in boiling water, from which, on cooling, it crystallises in small yet well-formed rhombic prisms of a fine yellow colour, with a tinge of violet. These crystals fuse at 148 — 150° C. to a brownish-yellow oil, which cannot be volatilised without decomposition, and is destroyed at a higher temperature with formation of yellow vapour. Although phenol-diazobenzol has the properties of an acid, forming with certain metals saline compounds, its acid character is so slightly pronounced, that it is not even capable of decomposing carbonates. On evaporating a solution of phenol-diazobenzol with aqueous carbonate of potassium to complete dryness, the former will be left behind unaltered. On evaporating it with aqueous ammonia, the whole of the ammonia is driven off. Treated with nitrate of silver, it yields a scarlet-red silver precipitate, which appears specially suited for determining the atomic weight of this compound. It deserves mention that phenol-diazobenzol is isomeric with azoxybenzide. The properties just described show conclusively, however, that it has nothing in common with the latter compound beyond the formula.

The second product of the above-mentioned reaction may usually be obtained perfectly pure by recrystallising it once or twice from strong alcohol, afterwards dissolving it in ether, and allowing the solution to evaporate spontaneously. Sometimes, however, the crystals are slightly contaminated with traces of a body which has to be removed by means of caustic potassa,† in

* Nitrosoethyline, recently described by Geuther and Kreutzhage, will probably come under the same class of compounds, since its composition may be expressed by the addition of the hypothetical diazohydride of ethyl and alcohol, viz.,

$$C_2H_4N_2 + C_2H_6O = C_4H_{10}N_2O.$$

† Instead of treating the mixture of the crude products of decomposition and carbonate of barium with hydrochloric acid, in order to remove the latter, the new compounds may be extracted with potassa, then precipitated with hydrochloric acid, and lastly, separated, as already described, by means of alcohol.

which the new compound is completely soluble, whilst the foreign substance remains behind as a brown resin. Hydrochloric acid precipitates it from the alkaline solution, and it can now be completely purified by crystallisation from alcohol or ether.

Its formation is explained by the equation

$$\underset{\text{Nitrate of diazobenzol.}}{3(C_6H_4N_2.NHO_3)} + H_2O = \underset{\text{New compound.}}{C_{18}H_{14}N_4O} + N_2 + 3NHO_3.$$

It may likewise be viewed as composed of phenol and diazobenzol, viz.,

$$2C_6H_4N_2 + C_6H_6O = C_{18}H_{14}N_4O.$$

and I would, therefore, propose the name *phenol-bidiazobenzol.*

This new compound crystallises in brownish-red needles or plates; it is readily soluble in ether, difficultly soluble in cold alcohol. Hot water dissolves it but very slightly. When heated, it deports itself like the compound previously described. It melts at 131° C. Phenol-bidiazobenzol is an almost perfectly neutral body. Its deportment with potassa (in which it dissolves readily, forming a ruby-red solution) reminds one, however, of the properties of an acid. Ammonia-water dissolves it with difficulty, and aqueous carbonate of potassa not at all. Dilute acids exert likewise no solvent action; concentrated acids, however, dissolve it with a blood-red colour. Decomposition ensues when the latter solutions are heated.

Action of Potassa upon Nitrate of Diazobenzol.

On mixing *diluted* aqueous solutions of these two bodies,* a yellow liquid is obtained, which possesses a peculiar aromatic odour, and soon begins to evolve nitrogen gas, a reddish-brown neutral substance being simultaneously formed. At the common temperature this reaction is very slow, and requires several weeks to be completed. If, however, heat is employed, the decomposition proceeds rapidly, and the reddish-brown substance is separated as a resinous, semifluid mass, quite insoluble in water, and only very

* The compound of hydrate of potassium and diazobenzol (page 46) does not seem to be formed in this case, as I was able to separate this substance only when very *concentrated* solutions of the nitrate of diazobenzol and potassa had been employed in its preparation.

slightly soluble even in boiling alcohol. Ether dissolves it readily. I have not been able to obtain this substance in crystals. By allowing its ethereal solution to evaporate spontaneously it is left behind in a resinous state. As a powder, it is very electric. Boiling with nitric acid produces a new yellowish crystalline body.

In order to purify the amorphous product of decomposition, I have first washed it thoroughly with water, then boiled it with alcohol, and finally dissolved it in ether; the substance remaining after the evaporation of the ether was submitted to analysis. The numbers obtained agree best with the formula

$$C_{24}H_{18}N_2O.$$

The formation of this substance may be expressed by the following equation:—

$$4(C_6H_4N_2.NHO_3) + H_2O = C_{24}H_{18}N_2O + 4NHO_3 + N_6.$$

If instead of an aqueous, an alcoholic solution of potassa be added to the nitrate of diazobenzol dissolved in water, the reaction which takes place is much more complicated. In this case, in addition to the reddish-brown body, two volatile substances are formed, viz., benzol and phenyl, $C_{12}H_{10}$, the hydrocarbon recently discovered by Fittig.* When the reaction is conducted in a retort, and heat is applied, the benzol passes over with the alcohol, and may be separated from it by the addition of water. The phenyl being less volatile, is obtained after the whole of the alcohol has distilled over; it condenses to a crystalline mass in the receiver. Repeated recrystallisations from alcohol render it quite pure, in white plates, resembling naphthaline, and fusible at 70° C. These properties leave no doubt as to its identity with the phenyl of Dr. Fittig, to whom I am indebted for a small portion of his substance, which resembles in every respect the body obtained as mentioned above.

The third product of the decomposition in question, viz., the amorphous brown substance, is left behind in the retort as a resinous mass.

From the foregoing observations it will be seen that potassa, in the presence of alcohol, causes simultaneously three different

* Ann. Ch. Pharm. cxxi, 363.

decompositions of the diazobenzol-molecule, which may be expressed as follows:—

$$\underset{\text{Diazobenzol.}}{C_6H_4N_2} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Benzol.}}{C_6H_6} + \underset{\text{Aldehyde.}}{C_2H_4O} + N_2.$$

$$2C_6H_4N_2 + C_2H_6O = \underset{\text{Phenyl.}}{C_{12}H_{10}} + C_2H_4O + N_4.$$

$$4C_6H_4N_2 + H_2O = \underset{\substack{\text{Reddish-brown}\\ \text{substance.}}}{C_{24}H_{18}N_2O} + N_6.$$

Action of Ammonia upon Aqueous Nitrate of Diazobenzol.

On adding diluted ammonia to an aqueous solution of this diazo-compound, a similar reaction takes place as when the potassa is employed. On treating the brown mass, however, with alcohol, it becomes evident that it consists of two bodies. The difficultly soluble portion is identical with the nitrogenous body previously described, as was proved by analysis.

The body accompanying it, which is readily soluble in alcohol, is obtained, by repeated crystallisation, in the form of small, light-yellow plates, which detonate on heating, and whose alcoholic solution gives precipitates with nitrate of silver and bichloride of platinum. This compound is, in fact, no other than the diazo-amidobenzol previously mentioned. The coincidence with this latter was so complete, that it appeared to me loss of time to analyse it. With regard to the first of the two products of decomposition, it is clear that its formation must be expressed by the same equation which illustrated the reaction with caustic potassa upon nitrate of diazobenzol, whilst the formation of the latter (the diazo-amidobenzol) is explained by assuming that a portion of the original compound is decomposed, in the following manner:—

$$\underset{\text{Nitrate of diazobenzol.}}{2(C_6H_4N_2.NHO_3)} + 3NH_3 = \underset{\text{Diazo-amidobenzol.}}{C_{12}H_{11}N_3} + N_2 + 2NH_4NO_3.$$

Two atoms of nitrogen in two equivalents of diazobenzol have, therefore, been simply replaced by one of ammonia.

Decomposition of the Platinum-salt of Diazobenzol, and of the Perbromide of Diazobenzol, by the action of heat.

When speaking of the platinum-salt, I had occasion to mention that it detonates when heated. By mixing it, however, with a large excess of perfectly dry carbonate of sodium,* and heating the whole in a retort on a sand-bath, it is quietly decomposed. The decomposition begins at a moderate heat, and is marked at first by evolution of gas, and subsequently by the distillation of an oily body. The residue in the retort consists of carbonate of sodium, metallic platinum, and chloride of sodium. The oily distillate contains chlorine. It is obtained perfectly pure by distilling once with chloride of calcium, and forms an almost colourless oil, which is heavier than water and has the odour of benzol. These properties, as well as the chlorine determination, prove that it is chlorobenzol, C_6H_5Cl†.

The formation of chlorobenzol may be expressed by the following equation :—

$$\underset{\text{Platinum-salt.}}{C_6H_4N_2.HCl.PtCl_2} = \underset{\text{Chlorobenzol.}}{C_6H_5Cl} + Pt + Cl_2 + N_2.$$

The platinum-salt of the bromide of diabenzol‡ is decomposed in an exactly similar manner. The resulting bromobenzol differs in no way from the bromobenzol obtained by Couper by the action of bromine upon benzol, as may easily be shown by converting it into nitrobromobenzol, which possesses all the properties of nitrobromobenzol prepared from coal-tar oil.

Bromobenzol can also be produced by the decomposition of perbromide of diazobenzol by heat, according to the equation

$$\underset{\text{Perbromide of diazobenzol.}}{C_6H_4N_2.HBr.Br_2} = \underset{\text{Bromobenzol.}}{C_6H_5Br} + N_2 + Br_2.$$

In order to decompose larger quantities of the perbromide of diazobenzol in this manner, it is likewise requisite to mix it first

* It is self-evident that other carbonates, such as carbonate of barium, calcium, &c., may be used instead of carbonate of sodium.

† In all probability it is identical with chlorobenzol obtained from benzol or phenol.

‡ This compound is obtained as an insoluble reddish-yellow precipitate, on mixing bibromide of platinum with an aqueous solution of nitrate of diazobenzol.

with a sufficient quantity of carbonate of sodium, to avoid a violent explosion.

By heating the mixture in a retort, bromobenzol is obtained almost perfectly pure. The perbromide, when heated with alcohol, likewise gives rise to a decomposition in accordance with the previous equations. Bromobenzol separates as a heavy oil on the addition of water to the alcoholic solution.

It deserves to be mentioned that all these reactions are very well defined, and that the amount of the products of decomposition corresponds almost theoretically with the quantities employed.

Appendix.

It may be of some interest to mention an experiment I made to obtain ethylated diazobenzol compounds. For this purpose I submitted nitrate of ethylaniline to the same reaction which produced from nitrate of aniline the nitrate of diazobenzol. I obtained a body crystallising, like the latter, in long needles. If this body had really been nitrate of ethyldiazobenzol, I should have expected to obtain, by boiling with water, a reaction according to the equation—

$$\underset{\text{Nitrate of ethyldiazobenzol.}}{C_6H_3(C_2H_5)N_2.NHO_3} + H_2O = \underset{\text{Ethylphenylic acid.}}{C_6H_5(C_2H_5)O} + NHO_3 + N_2.$$

It soon became evident, however, that the oily body produced was nothing else than ordinary phenylic acid; and since no other organic product of decomposition could be traced, I had to come to the conclusion that the above-mentioned crystals were nothing else than ordinary nitrate of diazobenzol. In order to decide this question, the gold-salt was prepared, and, after purifying it by recrystallisation from alcohol, the well-known golden, brilliant crystals were obtained, which gave, on analysis, numbers leading to the formula

$$C_6H_9N_2.HCl.AuCl_3.$$

The action of nitrous acid upon nitrate of ethylaniline may therefore be expressed by the equation—

$$\underset{\text{Nitrate of ethylaniline.}}{C_6H_6(C_2H_5)N.NHO_3} + NHO_2 = \underset{\text{Nitrate of diazobenzol.}}{C_6H_4N_2.NHO_3} + \underset{\text{Alcohol.}}{C_2H_6O} + H_2O.$$

Part V.

The peculiar and somewhat remarkable properties of the compounds derived from aniline in the manner previously described, have induced me to try whether bromaniline, nitraniline, &c., when similarly treated, would be converted into the corresponding substituted diazobenzols.

This I have succeeded in doing, and the new substances thus obtained exhibited all the properties which I found so characteristic of the normal diazobenzol-compounds. They are, if anything, more stable, owing, if I may so express myself, to the comparatively larger amount of solid and stable materials, combined with the extremely volatile and easily disturbed nitrogen. This property renders them better adapted for many experiments in which the non-substituted diazobenzol-compounds are liable to give rise to dangerous accidents. They are likewise remarkable for great beauty.

Nitrate of Diazobromobenzol, $C_6H_3BrN_2.NHO_3$.

This compound may be prepared by the action of nitrous acid gas either upon nitrate of bromaniline or upon diazo-amidobromobenzol, and in an exactly similar manner to the nitrate of diazobenzol. If an aqueous solution of nitrate of bromaniline be employed, nitrous acid gas must be passed through very rapidly at first, or else diazo-amidobromobenzol (even in the presence of much free nitric acid) begins to separate. This it is very difficult to convert into the desired compound in an aqueous solution. Nitrate of diazobromobenzol remaining comparatively constant in aqueous solutions, it is possible to concentrate them, without any great loss, by spontaneous evaporation in the open air, before precipitating with alcohol and ether. It can be obtained perfectly pure by repeatedly dissolving in alcohol and precipitating with ether, when it is obtained in the form of purely white scales which, when crystallising out rapidly, present themselves in the form of regular rhombic plates. These crystals, like those of nitrate of diazobenzol, are exceedingly soluble in water, difficultly so in strong alcohol, and almost insoluble in ether. They explode when heated, struck, or compressed, though not so readily nor with the same violence as the nitrate of diazobenzol, and they

can therefore be mixed without danger with oxide of copper and burnt in the usual mode of organic analysis.

The formation of nitrate of diazobromobenzol may be represented by the following equations :—

$$\underset{\text{Nitrate of bromaniline.}}{C_6H_6BrN.NHO_3} + HNO_2 = \underset{\text{Nitrate of diazobromobenzol.}}{C_6H_3BrN_2.NHO_3} + 2H_2O.$$

$$\underset{\text{Diazoamidobromobenzol.}}{C_{12}H_9Br_2N_3} + HNO_2 + 2NHO_3 = 2(\underset{\text{Nitrate of diazobromobenzol.}}{C_6H_3BrN_2.NHO_3}) + 2H_2O.$$

Sulphate of Diazobromobenzol, $C_6H_3BrN_2.SH_2O_4$.

The preparation of this compound from nitrate of diazobromobenzol and sulphuric acid corresponds so closely with that of the non-substituted (abromous) sulphate, that it may suffice simply to refer to the description already given of the preparation of the latter, and I will therefore restrict myself to a few remarks on its properties.

Sulphate of diazobromobenzol crystallises in very fine colourless prisms, which are very soluble in water, very difficultly soluble in alcohol, and almost insoluble in ether. The new body is comparatively stable, and can be crystallised from water without suffering the least decomposition, by allowing its solution to evaporate over sulphuric acid. Boiling water decomposes the compound, and heat causes it to explode.

Hydrobromate of Diazobromobenzol, $C_6H_3BrN_2.HBr$.

This compound is prepared either by decomposing an aqueous solution of the previous salt by means of a sufficient quantity of bromide of barium and spontaneous evaporation of the filtrate, or by the action of an ethereal solution of bromine upon an ethereal solution of diazo-amidobromobenzol. If prepared by this latter method, the new compound speedily separates in crystals, on account of its insolubility in ether, and is obtained pure by filtering off from the mother-liquor and washing the crystals with ether. Its formation may be expressed by the following equation :—

$$\underset{\text{Diazoamidobromobenzol.}}{C_{12}H_9Br_2N_3} + 4Br = \underset{\text{Hydrobromate of diazobromobenzol.}}{C_6H_3BrN_2.HBr} + \underset{\text{Tribromaniline.}}{C_6H_4Br_3N} + HBr,$$

The hydrobromate of diazobromobenzol forms pearly white shining scales which dissolve very readily in water; like the hydrobromate of diazobenzol, they are more difficultly soluble in alcohol, and quite insoluble in ether. In the dry state it can be preserved a long time without undergoing decomposition. On heating, it explodes almost as violently as the corresponding nitrate. By treating an aqueous solution with freshly precipitated chloride of silver, the hydrobromate is converted into the hydrochlorate of diazobenzol.

Perbromide of Diazobromobenzol, $C_6H_3BrN_2.HBr.Br_2$.

By treating an aqueous solution* of any one of the previously-described diazobromobenzol-compounds with excess of bromine-water, a crystalline orange precipitate speedily falls, increasing rapidly till all the diazobromobenzol has been precipitated. If too much bromine has been added, the precipitate becomes generally of an oily consistency, solidifying, however, to a yellow crystalline mass as soon as the mother-liquor has been removed and the excess of bromine allowed to evaporate spontaneously. In order to obtain the perbromide, thus prepared, in fine crystals, it is dissolved in the smallest possible quantity of warm, not boiling alcohol, from which it separates on cooling in yellow monoclinic prisms. A small portion only remains in the alcoholic mother-liquor, from which evaporation rarely recovers it, since it usually undergoes decomposition. It will, however, be seldom necessary to run this risk of losing part of the substance by recrystallisation, for the compound is almost perfectly pure from the very first, and at all events quite fit to be employed for the experiments to be described further on.

Under certain circumstances this perbromide is formed during the preparation of hydrobromate of diazobromobenzol from diazoamidobromobenzol, in which case the two compounds are readily separated from one another by washing with cold water. Perbromide of diazobromobenzol crystallises, as already remarked, in orange monoclinic prisms, insoluble in water, freely soluble in warm, difficultly so in cold alcohol, and very difficultly soluble in cold ether.

On boiling an alcoholic solution, decomposition ensues, and on

* The crude aqueous solution obtained by the action of nitrous acid upon the nitrate of bromaniline may conveniently be employed.

heating the crystals alone, they explode feebly, with disengagement of bromine vapour and nitrogen gas.

Platinum-salt of the Hydrochlorate of Diazobromobenzol, $C_6H_3BrN_2.HCl.PtCl_2$.

Bichloride of platinum, even from a very dilute solution of the nitrate or sulphate of diazobromobenzol, separates a mass of small yellow crystals, which appear under the microscope as fractured plates, and which are almost insoluble in every neutral solvent. They are stable at 100° C.

Gold-salt of the Hydrochlorate of Diazobromobenzol, $C_6H_3BrN_2.HCl.AuCl_3$.

This compound is precipitated from an aqueous solution of nitrate of diazobromobenzol on the addition of terchloride of gold, at first as a yellow oil, which, however, rapidly solidifies to a crystalline mass. The crystals are insoluble in water, but can be recrystallised from warm alcohol without much loss, and are thus obtained in the form of splendid, small, golden-yellow, shining plates.

Compound of Hydrate of Potassium with Diazobromobenzol, $C_6H_3BrN_2.KHO$.

On the addition of caustic potash to a concentrated solution of nitrate of diazobromobenzol, a lemon-yellowish precipitate of diazobromobenzol separates at first, but redissolves in excess of potash. On evaporation by means of a water-bath, the solution solidifies, when sufficiently concentrated, to a reddish-coloured crystalline paste of nitre and the new compound of hydrate of potassium and diazobromobenzol.

The latter is separated and purified exactly in the same manner to the analogous compound of diazobenzol. It differs from this compound in being precipitated from its alcoholic solution by means of ether as a white gelatinous mass, and not in the form of crystals. White plates are obtained by allowing its aqueous solution to evaporate on a watch-glass over sulphuric acid, which, however, turn red on keeping, owing to a partial decomposition.

Compound of Hydrate of Silver with Diazobromobenzol, $C_6H_3BrN_2.AgHO$.

This body is obtained as an almost white insoluble precipitate, very similar to the hydrate of silver with diazobenzol. I abstain from describing any more of the compounds of diazobromobenzol with metallic hydrates, since they entirely resemble the corresponding diazobenzol-compounds in every respect.

Diazobromobenzol, $C_6H_3BrN_2$,

is obtained in slender, bright-yellow needles by adding weak acetic acid to the compound of hydrate of potassium with diazobromobenzol, or as a bright yellow amorphous precipitate on the addition of dilute potassa to the aqueous solution of the nitrate of diazobromobenzol. In either case it is necessary to remove it speedily from the mother-liquor, and dry it rapidly over sulphuric acid.

Diazobromobenzol is an exceedingly dangerous compound; for the slightest pressure, or even touch with a rough object, causes it to go off in a fiery explosion almost exceeding in violence that of the nitrate of diazobenzol. Although much more stable than diazobenzol, it can be kept only for a short time in a perfectly unchanged condition. After being kept for some time, a reddish-brown residue is left, which no longer explodes even on heating, and it seems that the nitrogen has been gradually eliminated. Ether dissolves diazobromobenzol and causes a violent evolution of gas, frequently of such intensity as to give rise to explosions. When freshly prepared, this body is soluble in caustic potassa as well as in mineral acids, with formation of the previously-described saline bodies.

Compounds of Diazobromobenzol with Amido-Compounds.

Diazobromobenzol, like diazobenzol, can enter into combination with amido-bases and amido-acids. Since, however, these new bodies possess absolutely no fresh chemical interest, but resemble in every respect the amido-compounds of diazobenzol, it may suffice to mention a few only, as briefly as possible.

Diazo-amidobromobenzol, $\left\{\begin{matrix}C_6H_3BrN_2\\C_6H_6BrN\end{matrix}\right\}$,

separates in yellow needles or small plates when a concentrated aqueous solution of nitrate of diazobromobenzol is treated with an alcoholic solution of bromaniline. This compound was obtained by me on a former occasion* by the action of nitrous acid upon alcoholic aniline.

It needs no further proof that both methods furnish a product of identical properties. The action of aniline upon nitrate of diazobromobenzol gives rise to diazobromo-amidobenzol, which not only has the same empirical composition as the diazobenzol-amidobromobenzol ($C_{12}H_{10}BrN_3$) (page 49), but resembles it in every other respect. It would, no doubt, be of interest, to determine whether the two compounds are identical or only isomeric. I must, however, defer answering this question till a future opportunity.

Diazobromobenzol-amidobenzoic acid, $\left\{\begin{matrix}C_6H_3BrN_2\\C_7H_7NO_2\end{matrix}\right\}$.

This body is obtained as a yellow crystalline precipitate on mixing an aqueous solution of nitrate of diazobromobenzol and amidobenzoic acid, according to the equation

$$C_6H_3BrN_2.NHO_3 + 2C_7H_7NO_2 = \left\{\begin{matrix}C_6H_3BrN_2\\C_7H_7NO_2\end{matrix}\right\} + C_7H_7NO_2.NHO_3.$$

Nitrate of diazobromobenzol.	Amidobenzoic acid.	Diazobromobenzol-amidobenzol.	Nitrate of amidobenzoic acid.

Recrystallised from ether it forms roundish lumps of small needles or plates. In every other respect it is identical with diazobenzol-amidobenzoic acid.

Imidogen Compounds of Diazobromobenzol.

Diazobromobenzolimide, $\left.\begin{matrix}(C_6H_3BrN_2)''\\H\end{matrix}\right\}N.$

On mixing the yellow crystals of perbromide of diazobromobenzol with solution of ammonia, they are speedily converted into a yellowish oil, which, after a single distillation with water, is obtained in an almost colourless condition. This oil is diazobromobenzolimide in a perfectly pure state.

* Ann. Ch. Pharm. cxxi. 273.

If the temperature of the atmosphere be not too high, the oil usually solidifies after a short time. If this does not take place, artificial cold must be resorted to. The new compound is obtained for analysis by removing the water and drying over sulphuric acid.

Its formation is expressed by the following equation:—

$$\underset{\text{Perbromide.}}{C_6H_3BrN_2HBr} + 4NH_3 = \underset{\text{Diazobromobenzolimide.}}{\left.\begin{matrix}C_6H_3BrN_2\\H\end{matrix}\right\}N} + 3NH_4Br.$$

Diazobromobenzolimide presents itself generally as a white or slightly yellowish mass of small crystalline plates, which melt at about 20° C. to a heavy oil. It is insoluble in water, rather difficultly soluble in alcohol, and easily soluble in ether and benzol. It distils readily in the presence of water; heated alone it explodes feebly. Left exposed to the open air, it appears gradually to volatilise, giving off the same aromatic ammoniacal odour which characterises diazobenzolimide. It resembles the latter, moreover, in its behaviour with various reagents; caustic potassa, hydrochloric acid, and bromine have no action upon it, strong sulphuric and nitric acids decompose it readily.

By the action of ethylamine, aniline, &c., upon perbromide of diazobromobenzol, corresponding substitution-compounds of diazobromobenzolimide are obtained.

Ethyldiazobromobenzolimide $\left.\begin{matrix}(C_6H_3BrN_2)''\\C_2H_5\end{matrix}\right\}N$, forms a yellowish oil which does not solidify even when cooled much below 0° C.

Phenyldiazobromobenzolimide $\left.\begin{matrix}(C_6H_3BrN_2)''\\C_6H_5\end{matrix}\right\}N$, is obtained in the form of orange crystals.

Remarks on the products of Decomposition of the Compounds of Diazobromobenzol.

The great similarity existing between the properties of the diazobromobenzol-compounds and those of the corresponding abromous bodies, is likewise encountered in their products of decomposition obtained under similar circumstances; and I have, therefore, generally abstained from verifying the latter by analysis,

having restricted myself to bringing forward analytical numbers in a few cases only.

On heating an aqueous solution of nitrate or hydrobromate of diazobromobenzol, an evolution of nitrogen gas takes place, bromophenylic acid (which separates as a brownish oil of the odour of creosote) being simultaneously produced.

$$\underset{\text{Hydrobromate of diazobromobenzol.}}{C_6H_3BrN_2.HBr} + H_2O = \underset{\text{Bromophenylic acid.}}{C_6H_5BrO} + HBr + N_2.$$

Ebullition of nitrate of diazobromobenzol with alcohol gives rise to the formation of bromobenzol, which distils over with the vapour of alcohol, a yellow acid (probably bromodinitrophenylic) being left behind. Ammonia forms a yellow body with simultaneous production of diazo-amidobromobenzol, which, owing to its greater solubility in alcohol, can be readily separated from the former. The formation of diazo-amidobromobenzol takes place according to the formula

$$\underset{\text{Diazobromobenzol.}}{2C_6H_3BrN_2} + NH_3 = \underset{\text{Diazo-amidobromobenzol.}}{C_{12}H_9Br_2N_3} + N_2.$$

Sulphate of diazobromobenzol, when heated with sulphuric acid, is converted into a sulpho-acid, which is most probably disulphobromophenylenic acid, $C_6H_3Br.S_2H_4O_8$.

Nascent hydrogen, generated by the action of zinc upon sulphuric acid, in presence of an alcoholic solution of bromobenzolimide, converts the latter into bromaniline and ammonia.

$$\underset{\text{Diazobromobenzolimide.}}{C_6H_4BrN_3} + 8H = \underset{\text{Bromaniline.}}{C_6H_6BrN} + 2H_3N.$$

When the addition of water no longer gives rise to a precipitate, indicating that the whole of the imide has been decomposed, the bromaniline is most easily isolated by evaporating the alcoholic solution on a water-bath, and distilling with caustic potassa. Bromaniline then passes over in oily drops, which quickly solidify, and may be crystallised from alcohol in octahedra. These crystals, as well as the properties of the platinum-salt, prove it to be identical with the ordinary bromaniline.

By heating the platinum-salt of diazobenzol with carbonate of

sodium, chlorobenzol was obtained; so in like manner by the action of heat on the platinum-salt of hydrochlorate of diazobromobenzol, *chlorobromobenzol* is produced, according to the following equation:—

$$\underset{\text{Platinum-salt of diazobromobenzol.}}{C_6H_3BrN_2,HCl,PtCl_2} = \underset{\text{Chlorobromobenzol.}}{C_6H_4BrCl} + Pt + Cl_2 + N_2.$$

By pressing the crystals which condense in the neck of the retort between filter-paper, distilling a second time, and crystallising from alcohol, they are obtained sufficiently pure for analysis.

Chlorobromobenzol is rather difficultly soluble in alcohol, readily so in ether, and crystallises in white needles or plates from a hot saturated alcoholic solution on cooling, or by evaporation of the ethereal solution. The crystals possess a peculiar odour, resembling that of benzol.

The double salt of dibromide of platinum and hydrobromate of diazobromenzol is obtained in the form of ruby-red crystals, by mixing a tolerably concentrated aqueous solution of the diazo-salt with dibromide of platinum. This compound shows, as might be expected, a similar deportment. Like the preceding platinum-salt, it breaks up according to the equation,

$$\underset{\text{Platinum-salt of the hydrobromate of diazobromobenzol.}}{C_6H_3BrN_2.HBr.PtBr_2} = \underset{\text{Dibromobenzol.}}{C_6H_4Br_2} + Br_2 + N_2 + Pt.$$

Dibromobenzol is readily prepared also from the perbromide of diazobromobenzol by heating the latter alone,* or with carbonate of sodium, when it is decomposed according to the equation

$$\underset{\text{Perbromide of diazobromobenzol.}}{C_6H_3BrN_2HBr_3} = \underset{\text{Dibromobenzol.}}{C_6H_3Br_2} + Br_2 + N_2.$$

A still more convenient method of preparing dibromobenzol consists in the decomposition of the perbromide with alcohol, which is completed after a few minutes' boiling; and if too much

* Only small quantities must be employed, in order to prevent violent explosions. On heating the perbromide in a long-necked flask, the dibromobenzol condenses in the cold part of the vessel.

alcohol has not been employed, a large portion of the dibromobenzol separates at once in the form of crystals. The remaining portion is precipitated on the addition of water, in the form of a thick oil, which soon solidifies to a crystalline mass. After washing with a little alcohol and pressing between bibulous paper, this mass, together with the crystals first precipitated, is subjected to distillation. Dibromobenzol distils over as an almost colourless oil, which speedily solidifies.

Dibromobenzol very much resembles chlorobromobenzol in its various physical properties. It crystallises from ether in the form of rectangular prisms or small plates, which are frequently very regular and well formed, sometimes, however, agglomerated in various ways. It melts at 89°C.

The properties of the dibromobenzol prepared in the manner just described can leave no doubt that it is identical with the dibromobenzol described by Couper, and obtained by the action of bromine upon benzol. Although large quantities of dibromobenzol can be prepared by Couper's method with perhaps greater facility, it is always difficult to obtain the dibromo-compound quite free from tribromo-benzol, which is simultaneously formed.

The above method might be preferred in all cases when absolutely pure dibromobenzol is required, as, for instance, for certain physical purposes—the more so, since it invariably yields theoretical quantities. The same may be said of several other derivatives of benzol and its homologues, which are obtained from diazo-compounds to be described hereafter.

Diazodibromobenzol Compounds.

Nitrate of Diazodibromobenzol, $C_6H_2Br_2N_2.NHO_3$.

This compound is readily obtained by the action of a rapid current of nitrous acid upon an aqueous solution of nitrate of bromaniline containing free nitric acid. The liquid is allowed to evaporate spontaneously, the residue taken up with weak alcohol, and the new compound precipitated by means of ether. It can be recrystallised without loss from water or alcohol by evaporating the respective solutions below their boiling-points. Its aqueous solution remains remarkably constant. Continued boiling even for hours frequently leaves some of the substance undecomposed.

Nitrate of diazodibromobenzol crystallises in fine white prisms,

or elongated hexagonal plates. It does not detonate with the same violence as the corresponding bodies previously described.

Perbromide of Diazodibromobenzol, $C_6H_2Br_2N_2.HBr_3$.

This compound is formed by the addition of bromine-water to an aqueous solution of the nitrate of diazodibromobenzol, when it is precipitated in the form of fine long needles. On boiling with alcohol, and subsequently adding water, an oily substance is thrown down, which soon solidifies, and can be obtained perfectly pure by pressing the precipitate between bibulous paper, then distilling, and finally crystallising from alcohol. Thus purified it presents itself in the form of fine long silky needles. This substance is evidently tribromobenzol, presenting all the properties of that compound obtained by the distillation of $C_6H_6Br_6$ with alkalies by Lassaigne.*

Platinum-salt of the Hydrochlorate of Diazodibromobenzol.
$C_6H_2Br_2N_2.HCl.PtCl_2$.

It separates in small orange oval plates, which are difficultly soluble in water, on adding dichloride of platinum to the hydrochlorate.

Diazodibromobenzolimide, $\left.\begin{matrix}(C_6H_2Br_2N_2)''\\ H\end{matrix}\right\}N$.

Is easily obtained in crystals by mixing the perbromide,

$C_6H_2Br_2N_2.HBr_3$,

with ammonia. Repeated recrystallisation from hot alcohol yields it in the form of white needles, which melt at 62° C., and detonate slightly at a higher temperature. It is very little soluble in water, more soluble in hot alcohol, and very readily so in ether.

Diazochlorobenzol Compounds.

Perfect analogy exists between these bodies, as well as between the diazodichlorobenzol compounds, and the compounds just described, with regard not only to the modes of preparation from

* Rev. Scient., vol. v, p. 360.

chlorine and dichloroaniline, but also in respect to their various physical properties. I therefore abstain from entering into a minute description, and will simply enumerate some few experiments, which I hope will satisfactorily prove their great similarity.

Nitrate of Diazochlorobenzol, $C_6H_3ClN_2.NHO_3$,

crystallises in small white plates, which, on boiling with water, yield chlorophenylic acid in the form of a brownish oil possessing the odour of creosote.

Perbromide of Diazochlorobenzol, $C_6H_3ClN_2.HBr_3$,

forms yellow prisms, which are decomposed in boiling alcohol with formation of bromochlorobenzol, the composition of which is thus expressed, C_6H_4ClBr.*

Platinum-salt of the Hydrochlorate of Diazochlorobenzol, $C_6H_3ClN_2.HCl.PtCl_2$,

forms fine yellow needles. On heating with carbonate of sodium it yields dichlorobenzol, which is obtained, according as it crystallises slowly or rapidly, in long fine needles, or in elongated four-sided plates, possessing the same peculiar aromatic odour as the dibromobenzol.

Diazochlorobenzolimide, $\left.\begin{matrix}(C_6H_3ClN_2)''\\ H\end{matrix}\right\}N$, forms readily fusible crystals.

Diazochlorobenzol, $C_6H_3ClN_2$, is obtained as a highly explosive lemon-yellow precipitate.

Diazodichlorobenzol Compounds.

Nitrate of Diazodichlorobenzol presents itself in the form of white plates. The *perbromide,* $C_6H_2Cl_2N_2$, HBr_3, which is formed by the action of bromine-water, crystallises in yellow prisms; the platinum-salt in small, beautiful, yellow, very brilliant plates.

Diazo-iodobenzol Compounds.

It will suffice to give likewise only a short outline of these

* The bromochlorobenzol thus obtained is identical with the body described on page 74 as derived from $C_6H_3BrN_2.HCl.PtCl_2$.

bodies, owing to the great resemblance which usually exists between them and the compounds of diazobromobenzol, both in regard to their preparation and chemical deportment, and also with respect to their physical properties.

Nitrate of Diazo-iodobenzol, $C_6H_3IN_2.NHO_3$,

is prepared from nitrate of iodaniline, precisely like the corresponding bromo-compound, and crystallises in white needles or prisms, which are exceedingly soluble in water.

Sulphate of Diazo-iodobenzol, $C_6H_3IN_2,SH_2O_4$,

crystallises in small plates, which are easily soluble in water, difficultly so in alcohol.

Perbromide of Diazo-iodobenzol, $C_6H_3IN_2.HBr_3$,

forms small lemon-yellow slender plates.

On boiling this compound with alcohol, it yields bromoiodobenzol, C_6H_4BrI, which crystallises from ether or alcohol in large white plates, volatile without decomposition.

Platinum-salt of the Hydrochlorate of Diazoiodobenzol, $C_6H_3IN_2.HCl.PtCl_2$, forms small bright yellow clusters of needles.

Diazo-iodobenzolimide, $\left.\begin{matrix}(C_6H_3IN_2)''\\H\end{matrix}\right\}N$,

forms yellowish-white crystals, which are readily fusible, and pass over on distilling with water as a yellowish oil, soon solidifying. This likewise is of a peculiar aromatic ammoniacal odour.

Diazo-iodobenzol, $C_6H_3IN_2$,

is obtained as a yellow explosive precipitate.

Diazonitrobenzol Compounds.

The remarkable isomerism observed between α and β nitraniline, and hitherto left unexplained by any chemical theory, likewise extends, as I have shown upon a former occasion, to the double compounds which I have described as α and β diazo-amidonitrobenzol. This isomerism, however, is somewhat less striking, since

these bodies retain one-half the nitraniline required for their formation in the original condition, as will be clearly seen on examining the rational formula

$$\left\{\begin{matrix} C_6H_3(NO_2)N_2 \\ C_6H_4(NO_2)H_2N \end{matrix}\right\}$$

which I assign to these bodies. The simple diazo-compounds derived from these isomeric nitranilines cannot, however, be viewed similarly, and it was impossible therefore to decide *à priori* the question of their isomerism. The experiments presently to be described nevertheless leave no doubt that a similar isomerism exists between the several members of both series, and that, although of identical composition, they exhibit differences in their physical properties as striking as those observed between the original bases.

*α Diazonitrobenzol compounds.**

Nitrate of Diazonitrobenzol, $C_6H_3(NO_2)N_2HNO_3$.

The preparation of this compound by the action of nitrous acid upon α nitraniline is exactly similar to that of the analogous bodies already referred to. By gradually adding ether to its alcoholic solution till crystallisation commences, it is obtained in fine long needles, which, however, do not exhibit any distinct form of crystallisation.

This compound, like all the rest of the like bodies, is very readily soluble in water, more difficultly so in alcohol, insoluble in ether, and explodes with the same violence on heating.

Perbromide of α Diazonitrobenzol, $C_6H_3(NO_2)N_2.HBr_3$.

On mixing an aqueous solution of the former compound with bromine-water, this new body is speedily thrown down in slender orange prisms, which are almost insoluble in water, and scarcely soluble in ether. They dissolve, however, readily in warm alcohol, from which they are deposited, on cooling, in well-defined crystals.

* The *α* nitraniline employed for these experiments was obtained, according to Arppe's method, by the action of alkaline liquids upon nitrated anilides.

The *β* nitraniline was prepared, according to Hofmann and Muspratt's method, from dinitrobenzol by the reduction with sulphuretted hydrogen.

Platinum-salt of the Hydrochlorate of α Diazonitrobenzol, $C_6H_3(NO_2)N_2.HCl.PtCl_2$.

On the addition of chloride of platinum to a hot aqueous solution of the hydrochlorate of diazonitrobenzol, this double salt, which crystallises in long yellow needles, is precipitated. On recrystallising it from boiling water, in which it is soluble (although with difficulty), the crystals are obtained as prisms, frequently very well formed.

α Diazonitrobenzolimide, $\left.\begin{matrix}[C_6H_3(NO_3)N_2]'' \\ H\end{matrix}\right\}N$.

This compound is prepared by the action of ammonia upon perbromide of α diazonitrobenzol. By repeated recrystallisation from alcohol, it may be obtained in a perfectly pure state in the form of very brilliant yellow, rounded plates, which are so soluble in hot alcohol that a magma of crystals separates on cooling from a saturated solution. The crystals dissolve as readily in ether. In boiling water they fuse, producing a yellow oil but slightly soluble in water; the portion dissolved yields very fine, almost white crystals on cooling. The melting point of the crystals obtained by recrystallisation from alcohol was found to be 71° C. The substance explodes when heated a little above the melting point.

β Diazonitrobenzol compounds.

Nitrate of β Diazonitrobenzol, $C_6H_3(NO_2)N_2.NHO_3$,

is obtained from the nitrate of β nitraniline. The β does not differ much from the corresponding α compound in solubility; they, however, exhibit perceptible differences in the forms of their crystals, which in the β compound are prisms, frequently approaching the cubical form, whilst the crystals of the nitrate of α diazonitrobenzol are long needles of a somewhat unpronounced character.

Perbromide of β Diazonitrobenzol, $C_6H_3(NO_2)N_2.HBr_3$.

On treating an aqueous solution of the nitrate of β diazonitrobenzol with bromine-water, the new compound is thrown down

generally as an oil, which soon solidifies. It forms small plates or prisms of an orange colour, which seem to differ from the crystals of the α compound by their want of stability when treated with warm alcohol, and which I have scarcely ever been able to recrystallize. The perbromide of β diazonitrobenzol is also obtained by the action of bromine upon β diazo-amidonitrobenzol by suspending the latter in water and adding bromine till the whole is converted into a heavy brownish-red oil. The supernatant aqueous mother-liquor is decanted, and the excess of bromine allowed to evaporate spontaneously, when the oil solidifies to a crystalline mass.

Before, however, complete solidification occurs, thick yellowish-red prisms are frequently seen to shoot out, of about an inch in length, which consist of almost pure perbromide containing mere traces of tribromonitraniline, a body which forms in the reaction to nearly the same extent, as will be seen from the following equation:—

$$\underset{\beta\text{ diazoamidotribenzol.}}{C_{12}H_9(NO_2)_2N_3} + 8Br = \underset{\beta\text{ Perbromide.}}{C_6H_3(NO_2)N_2.HBr_3} + \underset{\text{Tribromonitraniline.}}{C_6H_3(NO_2)Br_3N} + 2HBr.$$

The adhering tribromnitraniline* can be removed by washing the finely pulverized crystals with ether, in which the perbromide is almost insoluble.

If no crystals are formed after the bromine has evaporated in the manner described, but only a crystalline mass of perbromide and tribromaniline, the latter is pressed between bibulous paper, and then washed with ether in order to separate the two compounds. This, however, cannot be done without incurring a considerable loss of perbromide, since by the action of the ether it is partly converted into nitrobromobenzol.

* In order to obtain the tribromnitraniline in a pure state, the ethereal solution is evaporated to dryness, and the residue dissolved by warm alcohol. Water is then added to the alcoholic solution till it becomes milky, and deposits crystals. These are thrown upon a filter, and then pressed between sheets of filter paper, in order to remove any adhering bromonitrobenzol, and purified further by recrystallisation from weak alcohol. Tribromnitraniline crystallizes in small, slightly yellowish plates, which cannot be sublimed without decomposition.

Platinum-salt of the Hydrochlorate of β Diazonitrobenzol, $C_6H_3(NO_2)N_2.HCl.PtCl_2$.

This compound crystallises likewise in needles or prisms resembling much the crystals of the α compound.

β Diazonitrobenzolimide, $\left.\begin{matrix}[C_6H_3(NO_2)N_2]'' \\ H\end{matrix}\right\}N$,

differs from the α compound by crystallising invariably in orange-coloured needles, which melt at 52° C., and consequently much below the melting point of the α compound. It is likewise somewhat soluble in hot water, from which it crystallises on cooling in whitish needles, closely resembling those of the α diazonitrobenzolimide recrystallised also from hot water. It has somewhat of the odour of nitrobenzol.

On the Products of Decomposition of the Diazonitrobenzol Compounds.

These, so far as my observations go, are decomposed under the influence of reagents like the other diazobenzol compounds; and their transformations may be expressed by corresponding equations. The nature of their products of decomposition may in fact be safely predicted before-hand, as the same isomerism which characterises the compounds already described is observable. It appeared of sufficient interest to trace them somewhat more fully. I could not have given the comparative history of the products of decomposition, however, without deviating too far from the main direction of this investigation, and I must therefore reserve for a future opportunity a more intimate acquaintance with these interesting bodies. A few illustrations will show how promising a harvest of interesting results may be expected from such an investigation. One peculiar fact deserves mention here. I had taken it for granted that the same relations would be exhibited between the isomeric diazonitrobenzol compounds and the isomeric acids of the formula $C_6H_5(NO_2)O$ (the nitrocarbolic acid of Hofmann and the isonitrocarbolic acid of Fritsche) as that observed between the compounds of diazobenzol and carbolic acid, and that their deportment would be represented by the equation,

$$\underset{\alpha\text{-}\beta\text{ Nitrate of diazonitrobenzol.}}{C_6H_3(NO_2)N_2.NHO_3} + H_2O = \underset{\alpha\text{-}\beta\text{ Nitrocarbolic acid.}}{C_6H_5(NO_2)O} + NHO_3 + N_2.$$

The assumption has not been verified. On boiling these diazonitrobenzol compounds with water, they are certainly decomposed, after some time, with evolution of nitrogen gas, but neither the α nor β compound furnishes under these circumstances either of the well-known phenylic substitutes. In both cases a brownish and easily fusible substance is obtained, which readily dissolves in alcohol and ether, but can in no manner be made to crystallise. I have not ascertained whether this substance deports itself differently according to its origin (from the α or β compound), nor have I analysed it; but, judging from the progress of its formation, and also from the weak acid properties it exhibits (dissolving in potassa and being reprecipitated by hydrochloric acid), I presume that its composition is probably represented by the formula

$$C_6H_5(NO_2)O.$$

On heating an alcoholic solution of the perbromide of α-diazonitrobenzol, it is readily decomposed according to the equation

$$\underset{\alpha\text{ perbromide.}}{C_6H_3(NO_2)N_2.HBr_3} = \underset{\text{Bromonitrobenzol.}}{C_6H_4(NO_2)Br} + N_2 + Br_2.$$

A portion of the bromonitrobenzol formed in this manner separates in crystals on cooling, provided the amount of alcohol employed has not been too large; the rest is precipitated on the addition of water. The crystals are purified by pressure between filter-paper and distillation, when they pass over as a slightly yellowish oil, which soon solidifies to a crystalline mass. The bromonitrobenzol thus prepared is difficultly soluble in cold, readily in hot alcohol and ether. It crystallises from these solvents in long almost white needles, which melt at 126° C., and have the odour of nitrobenzol.

If the perbromide of β-diazonitrobenzol is decomposed in a similar manner with boiling alcohol, and the solid product of decomposition which forms, is purified as described before, a compound is obtained to which the formula $C_6H_4(NO_2)Br$ must likewise be assigned, but which differs greatly in its physical appearance and properties from the former bromonitrobenzol. It crystallises from alcohol and ether, in which it seems to be more easily soluble,

in the form of well-made, slightly yellowish, or almost white rhombic prisms, sometimes also in plates, and melts at 56° C., or 70° below the melting point of the bromonitrobenzol derived from the α compound.

The existence of these bromonitrobenzols suggests the question whether one of them be not identical with the bromonitrobenzol prepared by Couper by the action of fuming nitric acid upon bromobenzol. Couper's description of this body appeared to me scarcely conclusive of its nature; and in order to decide this question, I have treated bromobenzol, prepared from coal-tar naphtha, with fuming nitric acid, and have compared the perfectly pure product, after repeated recrystallisations from alcohol, with the bromonitrobenzols prepared by my method. The striking coincidence between the crystalline form of Couper's compound and of the bromonitrobenzol corresponding to the α-nitraniline, which I will now call α-bromonitrobenzol, became at once perceptible; and since both compounds crystallise in white needles that could by no means be distinguished from one another, I felt justified in coming to the conclusion that both are identical. In order, however, to make quite sure, I have also determined the melting point of the respective compounds, and have found it uniformly at 120° C.*

They are acted upon in like manner by various reagents. When reduced in alcoholic solutions by sulphide of ammonium, they are both converted into bromaniline, which crystallises in octahedrons, and proves itself to be completely identical with that obtained from bromisatin or bromacetanilide by distillation with potash. Very different from this is the deportment of bromonitrobenzol (β bromonitrobenzol) prepared from perbromide of β diazonitrobenzol. On treating this compound with sulphide of ammonium, it is certainly also converted into bromaniline, but this base differs greatly from the above-described bromaniline. Ordinary bromaniline (which I would now designate as α bromaniline) crystallises, as is well known, in octahedra which melt at 57° C. The new base, however (the β bromaniline), forms an oil which does not solidify even in winter. The chemical deportment of both compounds is the same; they form, under like conditions, a series of derivatives which are of the same composition, and differ only in their physical properties.

* Couper states (Ann Ch. Phys. [3] lii, 309) that his compound melted below 90° C. This is evidently erroneous.

In order to establish the composition of the β bromaniline experimentally, I have analysed the hydrochlorate and its platinum-salt. *The hydrochlorate of β bromaniline* forms white, nacreous, brilliant plates, which are readily soluble in water and alcohol, and are rapidly coloured red when exposed to the air.

The Platinum-salt of the Hydrochlorate of β Bromaniline,
$C_6H_6BrN.HCl.PtCl_2$,

crystallises in yellow, often well-formed prisms, which are far more soluble in water than the slender highly lustrous plates of the platinum-salt of α bromaniline.

I need scarcely state that *nitrochlorobenzol* compounds corresponding to α and β nitrobromobenzol can readily be obtained by submitting the platinum-salts of α and β diazonitrobenzol to distillation with carbonate of sodium. These two bodies differ likewise most characteristically; α nitrochlorobenzol crystallises invariably in long, almost white needles which melt at 83° C., whilst β nitrochlorobenzol crystallises from its ethereal solution in thick columns, which fuse at 46° C. The former is converted by sulphide of ammonium into the ordinary (α) chloraniline, the latter into a new base (β chloraniline), which is distinguished by its remaining an oil at the common temperature. The platinum-salt presents itself in the form of yellow crystals, which differ likewise considerably in form and solubility from the small slender plates of the platinum-salt of α bromaniline. It may, I think, be safely deduced from these facts that two distinctly different series of compounds are obtained by the substitution of two atoms of hydrogen in benzol by two different elements, or groups of atoms, according to the manner in which this substitution is accomplished, and that these two series differ most distinctly in their physical properties, although their chemical composition is the same. The great differences between the melting-points form one of the most important means of distinction between the members of the two series. The melting points of series α lie considerably higher than those of the β series; sometimes a difference of 70° C. is observable, as will be seen by the accompanying Table.

	α Series.	β Series.
Bromonitrobenzol	126° C.	56° C.
Chloronitrobenzol	83° C.	46° C.
Nitraniline	141° C.	108° C.

	α Series.	*β* Series.
Bromaniline.....	57° C.	Liquid at the ordinary temperature.
Chloraniline.....		Liquid at the ordinary temperature.
Diazo-amidonitrobenzol..	245° C.	195° C.
Diazonitrobenzolimide ..	71° C.	53° C.

The compounds to which the experiments just described gave rise belonged exclusively to the aniline group. Now there could be little doubt that the homologues of aniline, and the similarly constituted bases, might be also converted into diazo-compounds. This I have confirmed by experiment, the more readily since it was to be foreseen that the decomposition of some of these compounds would give rise to the formation of certain bodies which could not have been obtained by the ordinary methods, *e.g.*, naphtylic alcohol, the existence of which, however, could not be doubted for a moment.

Diazotoluol Compounds.

These compounds exhibit considerable analogy, with regard to preparation, solubility, and many other properties, to the corresponding aniline derivatives. They seem, however, to be somewhat more constant, and to crystallise more readily.

Nitrate of Diazotoluol, $C_7H_6N_2.NHO_3$.

This substance is best prepared by the action of nitrous acid upon an aqueous solution of nitrate of toluidine, but it can also be obtained from diazo-amidotoluol. It forms long white needles, which are decomposed on boiling with water, according to the following equation:—

$$\underset{\text{Nitrate of diazotoluol.}}{C_7H_6N_2.NHO_3} + H_2O = \underset{\substack{\text{Cresyl-}\\\text{alcohol.}}}{C_7H_8O} + NHO_3 + N_2.$$

The other compounds are readily obtained from the nitrate in the ordinary manner.

Sulphate of Diazotoluol, $C_7H_6N_2.SH_2O_4$,

is obtained in brilliant needles, plates, or prisms, according to the

circumstances under which it crystallises. On heating it with sulphuric acid in the manner described when speaking of the sulphate of diazobenzol, it is converted into a sulpho-acid.

The barium-salt of this acid crystallises in long white needles, and consists of disulphotoluylenate of barium, which has the formula $C_7H_6S_2Ba_2O_7$.

Perbromide of Diazotoluol, $C_7H_6N_2.HBr.Br_2$,

is thrown down as a yellow oil, which, after evaporation of the excess of bromine, solidifies to a crystalline mass.

Platinum-salt of the Hydrochlorate of Diazotoluol, $C_7H_6N_2.HCl.PtCl_2$,

is precipitated from a dilute solution of the hydrochlorate of diazotoluol by means of bichloride of platinum, and forms fine yellow prisms. When ignited with soda, it yields an aromatic oil, chlorotoluol (C_7H_7Cl). It remains to be seen whether this oil is identical, or only isomeric with the chlorobenzyl discovered by Canizzaro.

Diazotoluol-amidobenzol, $\left\{\begin{matrix} C_7H_6N_2 \\ C_6H_5(H_2N) \end{matrix}\right.$,

is obtained by the action of aniline upon nitrate of diazotoluol. It crystallises in beautiful long yellow needles.

Diazonitranisol Compounds.

These compounds are nearly related to the diazonitrobenzol-compounds, both with regard to physical properties and their deportment with reagents. They are prepared also in a similar manner, and it is only necessary therefore to refer respecting their preparation to these analogous bodies.

Nitrate of Diazonitranisol, $C_7H_5(NO_2)N_2O.NHO_3$,

is obtained from nitrate of nitranisol. It separates from an alcoholic solution on addition of ether, forming small white plates, which are slowly decomposed on heating with water, giving rise to the formation of a brownish-red substance.

Perbromide of Diazonitranisol, $C_7H_5(NO_2)N_2O.HBr_3$,

forms small, yellow plates, which, on boiling with alcohol, furnish bromonitranisol ($C_7H_6(NO_2)Br$), crystallising in light-yellow opaque needles, which may be sublimed, and possesses the odour of nitrobenzol.

Diazonitranisolimide, $\left.\begin{matrix}(C_7H_5(NO_2)N_2O)''\\ H\end{matrix}\right\}N$,

crystallises in light-yellow needles, and has the odour of bitter almonds.

Platinum-salt of the Hydrochlorate of Diazonitranisol, $C_7H_5(NO_2)N_2O.HCl.PtCl_2$.

When precipitated from a moderately concentrated solution, it forms a yellow powder, which under the microscope is found to consist of fine needles. Recrystallised from boiling water, it is obtained in orange-red, well-formed prisms. On heating it with carbonate of sodium, chloronitranisol ($C_7H_6(NO_2)ClO$) distils over, which crystallises in fine, almost white needles.

Diazonaphtol Compounds.

Nitrate of Diazonaphtol, $C_{10}H_6N_2.NHO_3$,

is prepared by the action of nitrous acid on moist nitrate of napthalidine (amidonaphtol), an amorphous reddish-brown substance* being formed at the same time, which must be separated by filtration when the reaction is over. As nitrate of diazonaphtol is not precipitated from its aqueous solution by alcohol and ether, it is not so easily obtained in the solid state as the corresponding bodies previously described; if, however, its aqueous solution be allowed to evaporate spontaneously in a shallow vessel, long white needles are formed, which are very soluble in water and alcohol, and likewise very explosive.

Perbromide of Diazonaphtol, $C_{10}H_6N_2.HBr_3$,

is obtained in the form of orange-coloured crystals by the action of bromine-water upon the crude solution of the nitrate.

* Probably impure nitrate of diazonaphtol-amidonaphtol.

Platinum-salt of the Hydrochlorate of Diazonaphtol,
$C_{10}H_6N_2.HCl.PtCl_2$,

forms truncated, yellowish crystals, which are almost insoluble in water, alcohol, and ether.

Diazonaphtolimide, $\left.\begin{matrix}(C_{10}H_6N_2)''\\ H\end{matrix}\right\}N$,

passes over as a yellowish-coloured oil (which becomes brown when exposed to the air) by distilling with water the substance obtained by the action of ammonia upon the perbromide. It possesses somewhat the odour of naphtaline.

Observations on the Products of Decomposition of the Diazonaphtol Compounds.

After it had been shown that the products of decomposition of the diazonaphtol compounds so much resembled those of the other diazo-bodies, the intention of pursuing their study in all directions could not be entertained, especially since known bodies would frequently have formed the subject of such study. The decomposition of the perbromide, for instance, by means of alcohol gives rise to the formation of bromonaphtaline, that of the platinum-salt when ignited with carbonate of sodium to the formation of chlornaphtaline. It was thought, however, of sufficient importance to ascertain whether nitrate of diazonaphtol would split up according to the equation—

$$C_{10}H_6N_2.NHO_3 + H_2O = C_{10}H_8O + N_2 + NHO_3,$$

since the possibility of obtaining the long-sought-for naphtyl-alcohol presented itself. On boiling the solution of the nitrate of diazonaphtol, an immediate evolution of gas takes place, and a viscid violet-brown mass separates which remains on the filter when the solution is filtered hot.

The filtrate deposits generally small white plates, retaining, however, a portion of the substance dissolved, which can be recovered by shaking the aqueous solution with ether. On evaporating the ether, it remains behind as a violet-coloured oil which quickly solidifies. This latter, as well as the plates first deposited, is in fact almost pure naphtyl-alcohol, whilst the violet-brown

mass on the filter contains, besides naphtyl-alcohol, a considerable quantity of a reddish-brown body. In order to purify the naphtyl-alcohol, the united portions are treated with a cold solution of potassa, the residuary brown-red body* is filtered off, and the filtrate treated with acetic acid as long as precipitation ensues. Naphtyl-alcohol separates first as an oil, soon solidifying to a network of small plates, which are still somewhat violet-coloured. They are thrown on a filter, washed with cold water (which removes the mother-liquor), and then submitted to distillation.

This process must be repeated until the mass of crystals, which is invariably found deposited in the condensing-tube, is quite white, and fuses, on heating, to a limpid oil.

Naphtyl-alcohol crystallises in small white shining plates, melting at 91° C. to a colourless, highly refractive oil, which may be volatilised without decomposition. It is but slightly soluble in water, readily soluble in alcohol, ether, and benzol. When inflamed it burns with a thick smoky flame. Its formation and its physical properties prove its relationship with phenylic alcohol; it possesses a similar burning taste, and a creosote-like odour somewhat resembling that of naphtaline. The relation between it and phenylic alcohol is likewise indicated by its chemical deportment. It stands on the same narrow boundary line between acid and alcohol; and naphtyl-alcohol may, like phenol, be classified with alcohols or with acids. The strong bases form with the new alcohol (acid) a series of salts which are as unstable as those of phenylic acid, and are mostly decomposed even by the carbonic acid of the air. The potassium- or sodium-salt may also be obtained by the action of the respective metals upon the fused naphtylic acid with evolution of hydrogen. In both cases a crystalline saline mass is obtained which dissolves in water and alcohol. Basic acetate of lead produces in a solution of naphtyl-alcohol a white voluminous precipitate. An ammoniacal silver solution is decomposed, metallic silver being deposited. Nitric acid of sp. gr. 1·4 dissolves naphtyl-alcohol in the cold with evolution of red fumes. If the solution be boiled for some time and water added, a sparingly soluble yellow acid precipitates, whilst a second readily soluble acid is deposited in yellow crystals on evaporating the mother-liquor. The latter appears to be the picric

* This body is soluble in alcohol, to which it imparts a blood-red colour. On concentrating the alcoholic solution, reddish-brown indistinct crystals are deposited, which, on rubbing, acquire a green metallic lustre.

acid of the naphtyl group. By treating the aqueous solution of naphtyl-alcohol with bromine-water, it deposits bromonaphtylic acid in the form of an oil which speedily crystallises.

Many of the experiments described here and in the previous part of this investigation, were made in the laboratories of the Royal College of Chemistry, London, and of the University of Marburg; and it gives me great pleasure to express my sincere thanks to Professors Hofmann and Kolbe for the kind manner in which the laboratories of these institutions have been placed at my disposal.

Part VI.

All the diazo-compounds which have formed the subject of Parts IV. and V. of this inquiry are derived from monoamido-compounds. If the composition of the latter be again expressed by the general formula $C_xH_{(y-2)}(NH_3)''O_z$ (see page 36), it is at once perceived that the process of formation of the diazo-compounds is similar to the reaction which takes place by the action of nitrous acid on ammonia:

I. $\underset{\text{Monoamido-compound.}}{C_xH_{(y-2)}(NH_3)''O_z} + NHO_2 = \underset{\text{Diazo-compound.}}{C_xH_{(y-2)}(N_2)''O_z} + 2H_2O$*.

II. $\underset{\text{Ammonia.}}{(NH_3)''} + NHO_2 = \underset{\text{Nitrogen.}}{(N_2)''} + 2H_2O$.

By viewing the diamido-compounds in like manner as represented by the general formula $C_xH_{(y-4)}(NH_3)_2'',O_z$, it is evident that the action of nitrous acid may give rise to two decompositions:

1. $C_xH_{(y-4)}(NH_3)_2^{IV}O_z + NHO_2 = C_xH_{(y-4)}(NH_3)''(N_2)''O_z + 2H_2O$.

II. $C_xH_{(y-4)}(NH_3)_2^{IV}O_z + 2NHO_2 = C_xH_{(y-4)}(N_4)^{IV}O_z + 4H_2O$.

The hydrogen contained in one atom of ammonia can thus be replaced by nitrogen, or both atoms of ammonia present in the

* It must be borne in mind that nitrous acid acts upon the nitrates of the amido-compounds; if otherwise, the reactions would frequently give rise to the formation of diazoamido-compounds formerly described by me.

original compound may be replaced by nitrogen, giving rise to a tetrazo-compound.

Although this theory has not been fully confirmed by the action (presently to be described) that nitrous acid exerts on benzidine, since an intermediate compound, according to equation I could not be obtained, it is nevertheless highly probable that nitrogenous compounds in accordance with equation I, exist, and that further experiments with other diamido-compounds will confirm this view.

Action of Nitrous Acid upon Benzidine.

Benzidine, which Zinin, its original discoverer, expressed by the formula

$$C_6H_6N,$$

has been found, on further investigation by P. W. Hofmann, to have double the atomic weight first assigned to it, and to be a base capable of combining with two molecules of acid. Very recently Fittig has shown that it must be viewed as the diamido-compound of his newly discovered hydrocarbon, phenyl, and that it ought to be expressed by the rational formula $C_{12}H_8(NH_2)_2$, or $C_{12}H_6(NH_3)''_2$. I entirely agree with Fittig's view, but find it necessary to select for both compounds a somewhat modified nomenclature, in order to avoid the use of the same names for some derivatives of these bodies (which I shall have occasion to describe) already employed for several long known derivatives of phenylic acid. I propose, therefore, to designate Fittig's hydrocarbon, $C_{12}H_{10}$, as *diphenyl*, and to call benzidine, *diamidodiphenyl*.

Nitrate of Tetrazodiphenyl, $C_{12}H_6N_4.2NHO_3$.

This compound is most readily and copiously obtained by passing nitrous acid through a cold concentrated aqueous solution of nitrate of diamidobenzidol, when only traces of a brown amorphous body are formed, whilst from an alcoholic solution the latter is deposited in considerable quantities. When a sufficient current of gas has been passed through the solution, the brown body is separated by filtration, the filtrate mixed with twice its volume of strong alcohol, and ether added as long as any white crystals are deposited. By once more dissolving the crystals in a very small

quantity of water, and reprecipitating with alcohol and ether, they are obtained perfectly pure; it will be readily perceived that this mode of preparation closely resembles that for the preparation of nitrate of diazobenzol, which body presents a striking analogy to the nitrate of tetrazodiphenyl. The latter crystallises in white or slightly yellowish needles, which are readily soluble in water, more difficultly so in alcohol, and insoluble in ether. On heating they explode with the same violence as the analogous diazo-compound.

Sulphate of Tetrazodiphenyl, $C_{12}H_6N_4.3SH_2O_4$.

After mixing a concentrated aqueous solution of the nitrate of tetrazodiphenyl with a sufficient quantity of cold sulphuric acid, diluted previously with its own bulk of water, this new body separates, on the addition of strong alcohol, either in the form of a white crystalline powder, or in white needles. If alcohol does not completely precipitate it, ether must be added to complete its separation. It is very soluble in water. On heating it in the dry state, an explosion ensues.

Platinum-salt of the Hydrochlorate of Tetrazodipheynl, $C_{12}H_6N_4.2HCl.2PtCl_2$.

This salt is precipitated from a moderately dilute solution of the nitrate or sulphate by means of bichloride of platinum. It forms light-yellow very small narrow plates. By employing a very dilute solution, it is slowly deposited, in small, elongated, well-formed hexagonal plates. These crystals are almost insoluble in water, alcohol, and ether. Exposure to light during drying causes them to assume a slightly brown colour.

Perbromide of Tetrazodiphenyl, $C_{12}H_6N_4.2HBr.Br_4$.

This compound is formed on the addition of bromine-water to an aqueous solution of nitrate of tetrazodiphenyl, being precipitated in the form of round reddish crystals, which are collected on a filter, thoroughly washed with water, and dried without delay over sulphuric acid and caustic lime. They are thus obtained sufficiently pure for analysis. Further purification, indeed, is impossible, since this body is decomposed by dissolving in alcohol,

with evolution of gas. Even at the ordinary temperature it undergoes a gradual decomposition and evolves bromine, recognizable by its odour.

Tetrazodiphenyl-amidobenzol, $\left\{\begin{matrix} C_{12}H_6N_4 \\ C_6\ H_7N \\ C_6\ H_7N \end{matrix}\right\}$.

By adding aniline to an aqueous solution of nitrate of tetrazodiphenyl, this complex substance, corresponding to the diazoamidobenzol in the diazobenzol series, is at once separated as a yellow crystalline mass; by repeatedly washing with alcohol it is easily obtained in a pure state for analysis.

The formation of this new substance may be expressed as follows:—

$$\underset{\text{Nitrate of tetrazodiphenyl.}}{C_{12}H_6N_4.2NHO_3} + \underset{\text{Aniline.}}{4C_6H_7N} = \underset{\text{Tetrazodiphenyl-amidobenzol..}}{C_{24}H_{20}N_6} + \underset{\text{Nitrate of aniline.}}{2(C_6H_7N.NHO_3)}.$$

Tetrazodiphenyl-amidobenzol is insoluble in water, and, although very little soluble, even in boiling alcohol and ether, can be recrystallised from them. By this means lance-shaped crystals are obtained, which are generally grouped together in a star-like form. When heated they explode; boiled with mineral acids they are decomposed, with evolution of nitrogen gas.

Diphenylamide, $\left\{\begin{matrix} (C_{12}H_6N_4)^{IV} \\ H_2 \end{matrix}\right\} N_2$.

This body is obtained in crystals when the perbromide is acted upon by solution of ammonia. The crystals are purified by repeated recrystallisation from strong alcohol, when they are obtained in small, very brilliant, white, or slightly yellowish plates, insoluble in water, very difficultly soluble in cold alcohol, and only moderately soluble in ether. Boiling alcohol, however, dissolves them very readily, and yields on cooling a mass of crystals. The compound melts at 127° C. to a yellow oil, which is decomposed at a higher temperature, giving rise to slight explosions. It does not combine with acids or alkalies, and is perfectly neutral to test-paper. No change is produced even by boiling with concentrated hydrochloric acid, or with aqueous or alcoholic potash. It is decomposed, however, by nitric or strong sulphuric acid.

The formation of this compound may be expressed by the following equation :—

$$\underset{\text{Perbromide.}}{C_{12}H_6N_4.2HBr.Br_4}{}^{*} + 8NH_3 = \underset{\text{Tetrazodiphenylimide.}}{C_{12}H_8N_6} + 6NH_4Br.$$

It has been my endeavour to study somewhat more closely the compounds which tetrazodiphenyl forms with metallic hydrates, but all attempts to obtain them more definitely have failed; their preparation seems indeed to be beset with insurmountable difficulties. I omit a lengthened description of the unsuccessful attempts, and will merely show, by one instance, how tetrazodiphenyl can play the part of an acid. An aqueous solution of nitrate of tetrazodiphenyl, when mixed with caustic potash, yields a yellow liquid exhibiting such properties as might be looked for in a solution of the compound of hydrate of potassa with tetrazodiphenyl. On treating it with chloride of platinum, it gives rise to the formation of the platinum-compound above described, a proof that the tetrazodiphenyl remains unchanged in the alkaline solution. It is invariably decomposed on the application of heat, with evolution of gas and separation of a reddish-brown amorphous substance.

Products of Decomposition of the Compounds of Tetrazodiphenyl.

By applying the laws of classification now accepted by chemists to the tetrazotised derivatives of benzidine, specially taking into account their manner of formation and combination, these bodies must be classified with the diatomic compounds, whilst the respective diazo-compounds belong to the monatomic bodies. It has been of late a favourite subject of chemical research to trace the analogies which monatomic bodies exhibit under the influence of certain agents with polyatomic bodies. In illustration of this I may refer to the results obtained in the comparative study of the products of decomposition of the ethyl- and ethylene-alcohols, in order to show how simple are the laws which regulate these chemical transformations. The experimental results which I am able to adduce prove likewise

* Leaving aside the hydrobromic acid, this compound may be looked upon as the bromide of a tetratomic radical $(C_{12}H_6N_4)''''Br_4$.

that the decomposition of the tetrazo-compound gives rise to derivatives which differ in nothing from those obtained under similar circumstances from diazo-compounds, beyond the distinctive features imparted to them by the polyatomic nature of the compound from which they are derived.

Action of Water upon Nitrate of Tetrazodiphenyl.

An aqueous solution of this body, when left in a cold place, gradually undergoes spontaneous decomposition. When heated it gives rise to a copious evolution of nitrogen gas, with separation of two substances—one an amorphous brown, and the other a white crystalline body. An additional quantity of the latter is obtained when the liquid has become quite cold. It is easy to separate these two bodies by filtering off the acid mother-liquor, pressing the residue between bibulous paper, and repeatedly extracting with dilute alcohol, which takes up the crystalline substance and leaves the brown body undissolved; this latter being very probably identical with the brown compound obtained as a by-product in the formation of nitrate of tetrazobenzidol, and being moreover of a very unpromising nature, I have not pursued its study any further. The crystalline product of decomposition dissolved by the alcohol is obtained on evaporation as a yellowish crystalline mass, from which the last traces of the brown body are removed by repeatedly dissolving in ether, and recrystallising from dilute alcohol.

The formation of this compound, for which I propose the name of *diphenyl*-alcohol or *diphenylic* acid, takes place according to the equation

$$\underset{\text{Nitrate of tetrazodiphenyl.}}{C_{12}H_6N_4.2NHO_3} + 2H_2O = \underset{\text{Diphenyl-alcohol.}}{C_{12}H_{10}O_2} + 2NHO_3 + 4N.$$

Diphenyl-alcohol (diphenylic acid) crystallises in small white, or slightly tinged plates or needles, which possess slight solubility in water, but are soluble to any extent in alcohol and ether. It melts when heated, and can be sublimed in small quantities by heating it cautiously in a test-tube. It is thus obtained in the form of soft, white, very lustrous plates. The chemical deportment of diphenyl-alcohol shows it to be most closely allied to the class of compounds the best-known representative of which is phenylic alcohol. It may in fact be considered as the first biatomic representative of

this peculiar group of chemical componnds. The new alcohol is readily soluble in potash, and can be reprecipitated by the addition of an acid. Concentrated ammonia also dissolves it. On treating an ammoniacal solution with basic acetate of lead, a white voluminous precipitate ensues. Heated with ordinary strong nitric acid it is changed into a nitro-acid which crystallises out in yellow roundish crystals; the ammonium-salt of this acid crystallises in beautiful long needles.

Action of Alcohol upon Sulphate of Tetrazodiphenyl.

On heating a mixture of alcohol and sulphate of tetrazodiphenyl, violent decomposition takes place. The products formed are nitrogen, sulphuric acid, and a solid substance, which separates in small indistinct plates on mixing the alcoholic liquid (after the reaction is entirely over) with a large quantity of water. In order to free the precipitate from a trace of a brown substance, which likewise forms in the reaction, it is filtered off from the mother-liquor, dried, and then sublimed through paper, according to the method proposed by Gorup-Besanez. The substance is thus obtained in the form of perfectly white plates, which dissolve easily in ether and hot alcohol, and crystallise from the latter very much like naphtaline. At 70° C. it melts, yielding an oil, which distils at a higher temperature without decomposition. It possesses a peculiar aromatic odour like that of cinnamol and benzol combined.

Its chemical composition, combined with the before-mentioned physical properties, prove that the hydrocarbon is identical with the diphenyl described by Fittig.* Its formation may be described by the following equation :—

$$2(C_{12}H_6N_4.3SH_2O_4) + 4C_2H_6O = 2C_{12}H_{10} + 4C_2H_4O + N_8 + 6SH_2O_4.$$

Sulphate of tetrazodiphenyl. Alcohol. Diphenyl. Aldehyde.

Nitrate of tetrazodiphenyl is decomposed in a similar manner by boiling alcohol, but simultaneously the formation of a yellow

* If the diphenyl prepared according to my method, has not been previously sublimed through paper as described, it crystallises only in small indistinct silvery-white plates, which are so different from the large naphtaline-like plates described by Fittig, that they appear at first sight to be crystals of quite a different compound.

nitro-acid takes place, which stands probably to diphenylenic alcohol in the same relation as the nitrophenyl to phenylic alcohol (compare also the corresponding decomposition of nitrate of diazobenzol, p. 54).

Action of Sulphuric Acid upon Sulphate of Tetrazodiphenyl.

On heating sulphate of tetrazodiphenyl dissolved in a small quantity of oil of vitriol, a violent evolution of nitrogen gas is observed. The brown liquid which remains after the reaction has ceased, contains, besides the excess of sulphuric acid employed, two new sulpho-acids, which can be separated by means of their barium-salts. For this purpose the brown liquid is diluted with at least thirty times its volume of water, boiled, and saturated with carbonate of barium. The precipitated sulphate of barium is then filtered off, the saline solution evaporated to dryness on the water-bath, and the residue several times extracted with hot water. The portion remaining undissolved is the barium-salt of a new acid which I will call *tetrasulphodiphenylenic* acid; the soluble portion contains another new acid, for which the name *trisulphodiphenylenic* acid may be adopted.

I will first endeavour to give a brief description of the former. The barium-salt of this acid, obtained as before mentioned, being only very slightly soluble in water, could not well be purified by recrystallisation; I preferred therefore to convert it into the ammonium-salt, which served me as a starting-point for the preparation of all the saline compounds presently to be described. The ammonium-salt is readily obtained by decomposing the barium-salt with a solution of carbonate of ammonium. The mixture is heated for a short time, the insoluble carbonate of barium filtered off, and the filtrate concentrated on a water-bath till the ammonium-salt crystallises out on cooling. One recrystallisation from alcohol yields it in the form of perfectly pure white prisms.

Barium-salt of Tetrasulphodiphenylenic Acid, $C_{12}H_6.S_4H_2Ba_4O_{15}$.

On adding chloride of barium to a rather concentrated boiling solution of the ammonium-salt, this salt is precipitated in white needles or prisms; the crystals are allowed to subside, and, after

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the mother-liquor has been separated by filtration, repeatedly washed with cold water; in this manner they are obtained quite pure.

Dried over sulphuric acid, the salt retains four molecules of water of crystallisation.

If the ammonium-salt of tetrasulphophenylenic acid be treated with baryta-water, instead of chloride of barium, another barium-salt is formed, which, according to the subjoined barium-determination, has the composition $C_{12}H_6.S_4Ba_6O_{15}$. It is precipitated as a white amorphous powder, which, on washing with water, is converted into small prisms.

Silver-salt, $C_{12}H_6.S_4H_3Ag_3O_{15}$.

On mixing a concentrated solution of the ammonium-salt with an equally concentrated solution of nitrate of silver, separation of warty crystals of this salt takes place after some time. They may be purified by recrystallisation from water, in which they are easily soluble. The concentration of their solution must be conducted *in vacuo*.

When dried over sulphuric acid, it retains three molecules of water of crystallisation, which are given off at 100° C.

When describing disulphophenylenic acid (page 96), it was shown that it is capable of forming two series of salts, exhibiting to each other a relationship analogous to that of the metaphosphates and ordinary phosphates. Tetrasulphodiphenylenic acid behaves in a similar manner. Thus the salts previously described point most naturally to the conclusion that it is hexabasic, while the salts which will be presently mentioned indicate its capability of assuming also an octabasic character.

Lead-salt, $C_{12}H_6.S_4Pb_8O_{16}$.

When a boiling solution of tetrazodiphenylenate of ammonium is mixed with a solution of neutral acetate of lead, this salt is precipitated in the form of white needles. Repeated washings with water render it quite pure.

Basic Lead-salt, $C_{12}H_6.S_4Pb_8O_{16} + Pb_4O_2$.

This salt is obtained by treating the hot solution of the ammonium-salt with basic acetate of lead. It is a white amorphous precipitate.

Tetrasulphodiphenylenic acid is easily obtained in the free state, either by decomposing the lead- or silver-salt with sulphuretted hydrogen, or by treating the barium-salt with an equivalent quantity of sulphuric acid. The filtered aqueous solution is evaporated on a water-bath to a syrupy consistence, and placed over sulphuric acid; after some time white needles or plates are obtained, which are very soluble in water and alcohol, but not deliquescent in the air. I have not yet analysed this acid; but according to the above-mentioned salts it seems very probable that it can exist in two different states, as expressed by the formulæ $C_{12}H_6.S_8H_6O_{15}$ and $C_{12}H_6.S_8H_8O_{16}$.

The second compound (trisulphodiphenylenic acid) to which the reaction of sulphuric acid on sulphate of tetrazobenzidol gives rise deserves likewise a few passing remarks. The separation of its barium-salt from the barium-salt of tetrasulphodiphenylic acid by means of hot water has already been described. The aqueous extracts thus obtained, when sufficiently evaporated and allowed to cool, will generally solidify to a gelatinous mass, from which no distinct crystals can be obtained, even by repeated solution and evaporation. Crystallisation may, however, be effected thus: The gelatinous salt is converted into the ammonia-compound, by boiling with an aqueous solution of carbonate of ammonium. The excess of ammonia is removed by evaporation, and the crystalline residue dissolved in a little hot water and treated with a solution of chloride of barium. On cooling, warty crystals, or globular groups of small plates of the barium-salt, are obtained, which can be freed from the difficultly-soluble tetrasulphodiphenylate of barium with which it may still be contaminated, and also from the mother-liquor by repeated crystallisation from water.

Lead-salt, $C_{12}H_6.S_3Pb_6O_{12}$.

White amorphous precipitate obtained by treating a hot solution of the barium-salt with a solution of neutral acetate of lead.

Basic Lead-salt, $C_{12}H_6.S_3Pb_6O_{12}.Pb_4O_2$,

Precipitated from a solution of the ammonium- or barium-salt with basic acetate of lead. It scarcely differs in its properties from the previous salt.

Trisulphodiphenylenic Acid.

is obtained in the free state in exactly the same manner as tetrasulphodiphenylenic acid, which it resembles in every other respect. It is evident at a glance that its composition may also be expressed in two different ways, viz., $C_{12}H_6.S_3H_4O_{11}$, or $C_{12}H_6.S_3H_6O_{12}$.

In accordance with the experiment just described, the decomposition which tetrazodiphenyl undergoes by the action of sulphuric acid may be expressed by the following equations:—

$$\underset{\text{Tetrazodiphenyl.}}{C_{12}H_6N_4} + S_4H_8O_{16} = \underset{\text{Tetrasulphodiphenylenic acid.}}{C_{12}H_6S_4H_8O_{16}} + N_4.$$

$$\underset{\text{Tetrazodiphenyl.}}{C_{12}H_6N_4} + S_3H_6O_{12} = \underset{\text{Trisulphodiphenylenic acid.}}{C_{12}H_6.S_3H_6O_{12}} + N_4.$$

Decomposition of the Platinum-salt of Tetrazodiphenyl and of the Perbromide.

On mixing the platinum-salt of tetrazodiphenyl with from four to six times its weight of carbonate of sodium, and heating the mixture in a retort, a copious evolution of gas speedily ensues; and on increasing the heat, an oily body distils, which solidifies in the neck of the retort to a white mass. By pressing this body between bibulous paper, and repeated recrystallisation from boiling alcohol, it is obtained perfectly pure. Its composition is $C_{12}H_8Cl_2$, and its formation takes place thus:—

$$\underset{\text{Platinum-salt.}}{C_{12}H_6N_4.2HCl.2PtCl_2} = \underset{\text{New body.}}{C_{12}H_8Cl_2} + Cl_4 + Pt_2 + N_4.$$

This new body, which I will call *dichlorodiphenyl*, crystallises in white, usually well-formed prisms; it is difficult of solution even in boiling alcohol, but readily soluble in ether, and quite insoluble in water. It melts at 148° C. to a yellowish oil, which can be distilled without decomposition.

On heating in like manner the perbromide of tetrazodiphenyl with carbonate of sodium, a mixture of bromine and nitrogen gas is evolved, and on heating more strongly, an oily substance distils over, which quickly solidifies. It is obtained pure for analysis by repeated recrystallisation from ether.

This compound, which may be called *dibromodiphenyl*, resembles the previously described chlorine-compound; it crystallises likewise in well-formed prisms, which appear to be even more insoluble in alcohol and ether than the above, and melt at 164° C. This substance is obtained, moreover, by boiling the perbromide with alcohol, as in the following equation:—

$$\underset{\text{Perbromide.}}{C_{12}H_6N_4.H_2Br_2.Br_4} = \underset{\text{Dibromodiphenyl.}}{C_{12}H_8Br_2} + N_4 + Br_4.$$

The substance separates from the alcoholic solution on cooling in crystals; it is best purified by distillation.

Dr. Fittig informs me that he obtained a compound of like composition by acting with bromine upon diphenyl. The description of this new compound given by him applies so entirely to the dibromodiphenyl prepared by me, that no doubt remains of the identity of the bodies obtained by the two methods.

VI.—*Synthetical Researches on Ethers. No. 2. Action of Sodium and Isopropylic Iodide upon Ethylic Acetate.*

By E. Frankland, F.R.S., and B. F. Duppa, Esq.

In a former memoir* we described the consecutive action of sodium and the methylic, ethylic, and amylic iodides upon ethylic acetate. Two distinct classes of bodies resulted from these reactions, viz., 1st, bodies derived from the duplication of the molecule of ethylic acetate; and 2nd, bodies resulting from the substitution of one or more atoms of hydrogen in the methyl of acetic acid.

The general formula of the first of these classes of compounds may be thus written:—

$$\left\{\begin{matrix} \mathbf{C}OMe \\ \mathbf{C}R_2 \\ \mathbf{C}OEto \end{matrix}\right. .$$

In this formula R may be either hydrogen or a monad organic radical. These bodies, to which we gave the name *carboketonic*

* Phil. Trans. vol. clvi, p. 37, and Chem. Soc. J., vol. xix, p. 395.

ethers, are derived from corresponding compounds, in which sodium occupies the place either of one or of both atoms of R, the latter compounds being themselves obtained by the action of sodium upon ethylic acetate, according to the following equations :—

$$4\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right. + Na_2 = 2\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}NaH\\ \mathbf{C}OEto\end{matrix}\right. + 2EtHo + H_2:$$

Ethylic acetate. Ethylic sodacetone carbonate. Alcohol.

$$2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right. + Na_2 = \left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}Na_2\\ \mathbf{C}OEto\end{matrix}\right. + EtHo + H_2.$$

Ethylic acetate. Ethylic disodacetone carbonate. Alcohol.

The second class of bodies have the general formulæ :—

$$\left\{\begin{matrix}\mathbf{C}RH_2\\ \mathbf{C}OEto\end{matrix}\right. \qquad \left\{\begin{matrix}\mathbf{C}R_2H\\ \mathbf{C}OEto\end{matrix}\right. \qquad \left\{\begin{matrix}\mathbf{C}R_3\\ \mathbf{C}OEto\end{matrix}\right.$$

They are obtained by the action of the iodides of the positive compound radicals represented by R upon corresponding sodium compounds, viz. :—

$$\left\{\begin{matrix}\mathbf{C}NaH_2\\ \mathbf{C}OEto\end{matrix}\right. \qquad \left\{\begin{matrix}\mathbf{C}Na_2H\\ \mathbf{C}OEto\end{matrix}\right. \qquad \left\{\begin{matrix}\mathbf{C}Na_3\\ \mathbf{C}OEto\end{matrix}\right.$$

Ethylic sodacetate. Ethylic disodacetate. Ethylic trisodacetate.

These sodium compounds are produced, simultaneously with those belonging to the first class, by the action of sodium upon ethylic acetate. Thus ethylic disodacetate arises from the following reaction :—

$$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right. + Na_2 = \left\{\begin{matrix}\mathbf{C}Na_2H\\ \mathbf{C}OEto\end{matrix}\right. + H_2.$$

Ethylic acetate. Ethylic disodacetate.

By contact with the iodide of any radical C_nH_{2n+1}, these compounds exchange their sodium for an equivalent amount of C_nH_{2n+1}, thus :—

$$\left\{\begin{matrix}\mathbf{C}Na_2H\\ \mathbf{C}OEto\end{matrix}\right. + 2C_nH_{2n+1}I = \left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})_2H\\ \mathbf{C}OEto\end{matrix}\right. + 2NaI.$$

Ethylic disodacetate. Ethylic salt.

If, in these formulæ, $n = 0$ ethylic acetate $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right.\right)$ is reproduced, but if n be a positive integer, an ethereal salt is obtained of the molecular weight of ethylic acetate increased by one, two, or three times C_nH_{2n}.

We have now extended these reactions to isopropylic iodide, for an ample supply of which we are indebted to Professor Wanklyn. The sodium compounds derived from ethylic acetate and prepared as described in our former communication,* were treated with excess of isopropylic iodide, and digested for 24 hours in a water-bath, an upright Liebig's condenser being attached to the flask containing the materials. At the end of this time, the products volatile at 100° were distilled off. They consisted chiefly of ethylic acetate, isopropylic iodide, and isopropylic ethylic ether $\left(\left\{\begin{matrix}\mathbf{C}Me_2H\\ O\\ \mathbf{C}MeH_2\end{matrix}\right.\right)$. Water acidulated with sulphuric was now added, until the contents of the flask exhibited a decidedly acid reaction. They were then submitted to distillation. A sweet-smelling oily liquid passed over along with water; it was separated, dried over calcic chloride, and distilled. It began to boil at about 70° C., and the thermometer rose eventually to 300° C. Below 100° the distillate, which consisted chiefly of ethylic acetate, isopropylic iodide, and alcohol, contained an abundance of two products, one boiling at about 135° C., and the other at about 200° C. The latter gave with baric hydrate the characteristic reaction of a carboketonic ether, whilst the former possessed in a high degree the peculiar odour of ethylic valerate.

Ethylic Isopropacetone Carbonate.

The section of the above distillate boiling at about 200°, yielded on careful rectification, a liquid boiling constantly at 201° C. Submitted to analysis this liquid gave the following results:—

I. ·3402 grm. gave ·7826 grm. carbonic anhydride, and ·2896 grm. water.

II. ·1861 grm gave ·4274 grm. carbonic anhydride, and ·1594 grm. water.

* Chem. Soc. J., vol. xix, p. 396.

These numbers lead to the formula

$$C_9H_{16}O_3,$$

as seen in the annexed comparison of calculated and experimental numbers:—

	Calculated.		Found.		
			I.	II.	Mean.
C_9....	108	62·79	62·73	62·63	62·68
H_{16}...	16	9·30	9·45	9·51	9·48
O_3....	48	27·91	..	..	27·84
	172	100·00			100·00

This product of the action of sodium and isopropylic iodide upon ethylic acetate is therefore homologous with ethylic methacetone carbonate and ethylic ethacetone carbonate, obtained in the corresponding reactions with ethylic and methylic iodides, as is evident on inspection of their respective formulæ:—

$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}MeH;\\ \mathbf{C}OEto\end{matrix}\right.$	$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}EtH;\\ \mathbf{C}OEto\end{matrix}\right.$	$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}\beta PrH^{*}.\\ \mathbf{C}OEto\end{matrix}\right.$
Ethylic methacetone carbonate.	Ethylic ethacetone carbonate.	Ethylic isopropacetone carbonate.

Ethylic isopropacetone carbonate results from the action of isopropylic iodide upon ethylic sodacetone carbonate, according to the following equation:—

$$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}NaH\\ \mathbf{C}OEto\end{matrix}\right. + \beta PrI = \left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}\beta PrH\\ \mathbf{C}OEto\end{matrix}\right. + NaI.$$

Ethylic sodacetone carbonate. Isopropylic iodide. Ethylic isopropacetone carbonate.

Ethylic isopropacetone carbonate is a colourless and somewhat oily liquid, of an odour resembling damp straw, and a pungent taste. It is insoluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity at 0° C. is ·98046. It boils at 201° (barometer ·7584 metre), and distils without decomposition. A determination of its vapour-density by Gay Lussac's method gave the following results:—

* $\beta Pr = \mathbf{C}Me_2H$.

Weight of ethylic isopropacetone carbonate ..	·1248 grm.
Observed volume of vapour	34·9 c. c.
Temperature of bath	225° C.
Height of barometer	767 m.m.
Difference of heights of mercury inside and outside of tube	136 „ „
Height of spermaceti column reduced to millimetres of mercury	16·6 „ „

From these data the weight of one litre of ethylic isopropacetone carbonate is calculated to be 85·6 criths, or its specific gravity compared with air taken as unity is 5·92. Theoretically the vapour of a body of this composition, and occupying 2 vols., ought to give the numbers 86 criths and 5·94. Ethylic isopropacetone carbonate has no action upon polarized light. Boiling aqueous solutions of potash and soda rapidly decompose ethylic isopropacetone carbonate, which also suffers a similar decomposition when boiled with baryta-water. Baric carbonate is in the latter case precipitated, and a volatile liquid possessing a camphoric odour produced. This liquid, washed with salt and water and dried over quicklime, boiled constantly at 114° C., and yielded on analysis the following numbers:—

I. ·2032 grm. gave ·5338 grm. carbonic anhydride and ·2250 grm. water.

II. ·1722 grm. gave ·4550 grm. carbonic anhydride and ·1890 grm. water.

The following comparison shows that these numbers agree closely with the formula:—

$$C_6H_{12}O.$$

		Found.		
	Calculated.	I.	II.	Mean.
C_6	72	71·64	72·06	71·85
H_{12}	12	12·30	12·19	12·24
O	16	..	..	15·91
	100			100·00

This result is exactly homologous with those obtained in the corresponding reactions, which we have previously described. For reasons given in the memoir above cited, we regard

this body as acetone in which one atom of hydrogen has been displaced by isopropyl:

$$\begin{cases} \mathbf{C}H_3 \\ \mathbf{C}OMe \end{cases} \qquad \begin{cases} \mathbf{C}\beta PrH_2 \\ \mathbf{C}OMe \end{cases}$$

Acetone. Isopropacetone.

and we propose for it the name *isopropacetone.*

Isopropacetone is produced by the action of baryta-water upon ethylic isopropacetone carbonate according to the following equation:—

$$\begin{cases} \mathbf{C}OMe \\ \mathbf{C}\beta PrH \\ \mathbf{C}OEto \end{cases} + \mathbf{Ba}Ho_2 = \mathbf{C}OBao'' + EtHo + \begin{cases} \mathbf{C}\beta PrH_2 \\ \mathbf{C}OMe \end{cases}.$$

Ethylic isopropacetone carbonate. — Baric hydrate. — Baric carbonate. — Alcohol. — Isopropacetone.

Isopropacetone is a colourless, transparent, and very mobile liquid, possessing a powerful camphoric odour and a burning taste. It is very sparingly soluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity is ·81892 at 0° C. It boils at 114° C., with the barometer at ·7584 meter. A determination of its vapour-density gave the following numbers:—

Weight of isopropacetone	·1160 grm.
Observed vol. of vapour	43·9 c. c.
Temperature of bath	137° C.
Height of barometer	764 m.m.
Difference of heights of mercury inside and outside of tube	112 m.m.
Height of spemaceti column reduced to millimetres of mercury.....	16·8 m.m.

Hence one litre of the vapour weighs 50·1 criths, and its sp. gr. is 3·48. A two-volume vapour of the above formula requires the numbers 50 criths and 3·455.

Isopropacetone does not reduce boiling solution of argentic nitrate. Agitated with a concentrated solution of hydric sodic sulphite, it solidifies to a splendid mass of white crystals.

A ketone of the same composition (methyl valeral) has been obtained by Williamson in distilling a mixture of potassic acetate and valerate. This body, which, for reasons mentioned below, we regard as isomeric with isopropacetone, boils at

120° C. Isopropacetone is also isomeric with ethyl-butyral boiling at about 128° C.

Amongst the products of the action of sodium and isopropylic iodide upon ethylic acetate there ought to be a carboketonic ether containing two atoms of isopropyl, and having a constitution analogous to that of ethylic diethacetone carbonate.

$$\begin{cases} \mathbf{C}OMe \\ \mathbf{C}Et_2 \\ \mathbf{C}OEto \end{cases} \qquad \begin{cases} \mathbf{C}OMe \\ \mathbf{C}\beta Pr_2 . \\ \mathbf{C}OEto \end{cases}$$

Ethylic diethacetone carbonate. Ethylic di-isopropacetone carbonate.

Unmistakeable indications of the existence of this body were noticed, but we have not attempted to isolate it.

Isopropacetic Acid.

The section of ethereal product described above as boiling at about 135° C. yielded, on further distillation, a considerable quantity of a liquid boiling constantly at 134° to 135° C. This liquid was submitted to analysis, and gave the following numbers:—

I. ·1836 grm. gave ·4361 grm. carbonic anhydride and ·1832 grm. water.

II. ·2786 grm. gave ·6602 grm. carbonic anhydride and ·2722 grm. water.

These results lead to the formula

$$C_7H_{14}O_2,$$

as will be evident from the following comparison of analytical and calculated numbers:—

	Calculated.		I.	II.	Mean.
C_7	84	64·62	64·78	64·63	64·70
H_{14}....	14	10·77	11·08	10·86	10·97
O_2	32	24·61	..	..	24·33
	130	100·00			100·00

The formula and reactions of this body prove it to be *ethylic isopropacetate;* that is, ethylic acetate, in which one 1 atom of non-ethylic hydrogen has been displaced by isopropyl: –

$$\left\{\begin{matrix}\mathbf{C}\beta\mathrm{PrH}_2\\ \mathbf{C}\mathrm{OEto}\end{matrix}\right.$$

Ethylic isopropacetate is produced from ethylic sodacetate by the following reaction:—

$$\left\{\begin{matrix}\mathbf{C}\mathrm{NaH}_2\\ \mathbf{C}\mathrm{OEto}\end{matrix}\right. + \beta\mathrm{PrI} = \left\{\begin{matrix}\mathbf{C}\beta\mathrm{PrH}_2\\ \mathbf{C}\mathrm{OEto}\end{matrix}\right. + \mathrm{NaI}.$$

Ethylic sodacetate. Isopropylic iodide. Ethylic isopropacetate.

Ethylic isopropacetate is a colourless, transparent, and oily liquid, nearly insoluble in water, soluble in alcohol and ether, and undistinguishable in odour from ethylic valerate (*ethylic propacetate*), with which, as we have proved below, ethylic isopropacetate is isomeric. Its specific gravity is ·8882 at 0° C. and ·87166 at 18° C. It boils at 134° to 135° C. (barom. ·7584 metre). A determination of its vapour-density gave the following numbers:—

Weight of ethylic isopropacetate	·1396 grm.
Observed volume of vapour	41·56 cbc.c.
Temperature of bath	147° C.
Height of barometer	751·4 m.m.
Difference of heights of mercury inside and outside of tube.....	110·5 m.m.
Height of spermaceti column reduced to millimetres of mercury	17·9 m.m.

Hence the sp. gr. of the vapour is 4·64 or one litre weighs 67·1 criths. A two-volume vapour of the above formula requires the numbers 4·49 and 65 criths.

Ethylic isopropacetate is readily decomposed by alcoholic potash, potassic isopropacetate being formed. The alcoholic liquid so produced being mixed with water and evaporated to dryness, left a saline residue, which was treated with dilute sulphuric acid and submitted to distillation. An oily liquid passed over which strongly reddened litmus paper. This liquid separated from the aqueous layer below, was dried, and then boiled constantly at 175° C. Submitted to analysis it gave the following results:—

I. ·1858 grm. gave ·3991 grm. carbonic anhydride and ·1663 grm. water.

II. ·3322 grm. gave ·7152 grm. carbonic anhydride and ·2886 grm. water.

These numbers agree with the formula

$$C_5H_{10}O_2 \text{ or } \begin{cases} \mathbf{C}\beta\mathrm{Pr}H_2 \\ \mathbf{C}OHo \end{cases}$$

as shown by the following comparison:—

	Calculated.		Found. I.	Found. II.	Found. Mean.
C_5	60	58·82	58·58	58·72	58·65
H_{10}....	10	9·80	9·94	9·65	9·80
O_2	32	31·38	..	..	31·55
	102	100·00			100·00

Isopropacetic acid is a colourless, transparent, oily liquid, somewhat soluble in water, to which it imparts both its odour and strong acid reaction. Its odour cannot be distinguished from that of valeric acid prepared from amylic alcohol. Its specific gravity is ·95357 at 0° C. It boils at 175° C., and a determination of its vapour-density gave the following numbers:—

Weight of isopropacetic acid	·1163 grm.
Observed volume of vapour.....	50·77 c. c.
Temperature of bath.....	215° C.
Height of barometer.....	755·5 m.m.
Difference of heights of mercury, inside and outside of tube	80·0 m.m.
Height of spermaceti column, reduced to millimetres of mercury.....	16·9 m.m.

Hence the specific gravity of the vapour is 3·479, or one litre weighs 50·4 criths. A two-volume vapour of the above formula requires the numbers 3·52 and 51 criths.

Isopropacetic acid dissolved in water, boiled with argentic carbonate and filtered, gives, on evaporation in vacuo, beautiful and very light pearly scales, which are tolerably permanent in light, and exhale an odour of the acid. 100 parts of water at 10° C. dissolve ·187 parts of this salt. Dried over sulphuric acid, this salt yielded, on analysis, the following numbers:—

I. ·1800 grm. gave ·1876 grm. carbonic anhydride, ·0700 grm. water, and ·0934 grm. silver.

II. ·2194 grm. gave ·2312 grm. carbonic anhydride, ·0883 grm. water, and ·1136 grm. silver.

These numbers agree closely with the formula

$$C_5H_9AgO_2 \text{ or } \begin{cases} \mathbf{C}\beta\mathrm{PrH}_2 \\ \mathbf{C}\mathrm{OAgo} \end{cases}$$

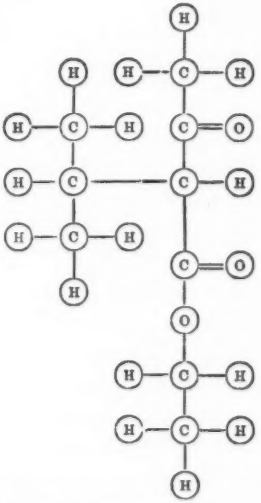
as the subjoined comparison shows:—

		Calculated.	I.	II.	Mean.
C_5	60	28·70	28·42	28·74	28·58
H_9	9	4·31	4·32	4·47	4·40
Ag	108	51·67	51·88	51·77	51·82
O_2	32	15·32	..	..	15·20
	209	100·00			100·00

In our former memoir* we have entered fully into the chemical relations of the products derived from the duplication of the molecule of ethylic acetate; when the latter is acted upon, first by sodium and afterwards by methylic or ethylic iodide. The corresponding reaction with isopropylic iodide described in the foregoing pages, is so completely homologous with those exhibited by methylic and ethylic iodides, as to render it superfluous to enter into any theoretical considerations relating to the production of ethylic isopropacetone carbonate or of the ketone derived from it; but, in order to prevent any misapprehension of our views concerning the constitution of these bodies, we here subjoin their graphic formulæ:—

$$\begin{cases} \mathbf{C}\mathrm{OMe} \\ \mathbf{C}(\mathbf{C}\mathrm{Me}_2\mathrm{H})\mathrm{H} \\ \mathbf{C}\mathrm{OEto} \end{cases} = \begin{cases} \mathbf{C}\mathrm{OMe} \\ \mathbf{C}\beta\mathrm{PrH} \\ \mathbf{C}\mathrm{OEto} \end{cases} =$$

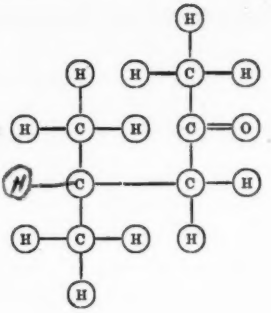
Ethylic isopropacetone carbonate.



* Phil. Trans., clvi, p. 37, and Jour. Chem. Soc, vol. xix., 419.

$$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}(\mathbf{C}Me_2H)H_2\end{matrix}\right. = \left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}\beta PrH_2\end{matrix}\right. =$$

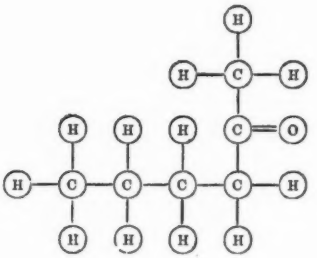
Isopropacetone.



We have already mentioned that isopropacetone is isomeric with the ketone, methyl-valeral, obtained by Williamson, in distilling a mixture of potassic acetate and valerate, and also with ethyl-butyral. The origin of methyl-valeral indicates the probable constitution of that body, whilst the cause of its isomerism with isopropacetone is evident from the following constitutional formulæ :—

$$\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}(\mathbf{C}EtH_2)H_2\end{matrix}\right. = \left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}PrH_2\end{matrix}\right. =$$

Methyl-valeral.



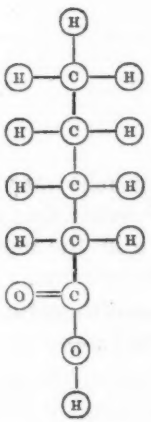
Isopropacetone differs from methyl-valeral in its boiling point, which is 6° C. lower, as might be anticipated from the boiling points of isopropylic and propylic alcohols, which differ by 9° C. in the same direction. This difference of boiling point is doubtless due to the difference in the constitution of the radicals, propyl and isopropyl, the former being a normal and the latter a secondary radical, and, as has been shown by Kolbe and ourselves, normal compounds always boil at a higher temperature than their secondary isomers. The temperatures of ebullition of the two radicals doubtless differ much more widely than those of their respective compounds; and as the atomic weight of the compound becomes proportionally greater with regard to that

of the radical, this difference becomes less and less appreciable. Unfortunately we are not acquainted with the specific gravity of methyl-valeral, nor with its deportment towards hydric sodic sulphite. The production of ethyl butyral by the destructive distillation of calcic butyrate permits of no conclusions being drawn as to its rational constitution. Its behaviour with hydric sodic sulphite is not known, but its boiling point, 14° C. higher than that of isopropacetone, proclaims its non-identity with the latter substance.

Two acids having the composition and atomic weight of valeric acid are now known, viz., valeric acid or propacetic acid obtained by the oxidation of normal amylic alcohol, and isopropacetic acid produced as above described. To these may be added a third, which we have had for some time under investigation, and the history of which we hope soon to be able to lay before the Society. This last acid is produced by the substitution of the three atoms of hydrogen, in the methyl of acetic acid, by three atoms of methyl. These acids are represented by the following constitutional formulæ :—

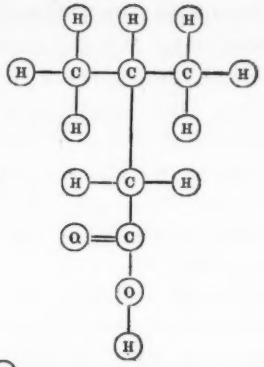
$$\left\{\begin{matrix}\mathbf{C}\mathrm{PrH_2}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. = \left\{\begin{matrix}\mathbf{C}(\mathbf{C}\mathrm{EtH_2})\mathrm{H_2}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. =$$

Valeric acid



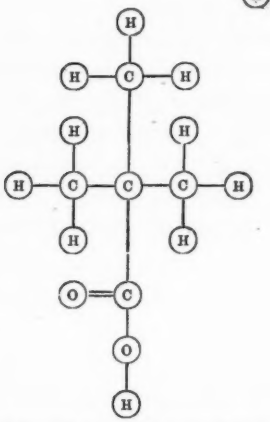
$$\left\{\begin{matrix}\mathbf{C}\beta\mathrm{PrH_2}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. = \left\{\begin{matrix}\mathbf{C}(\mathbf{C}\mathrm{Me_2H})\mathrm{H_2}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. =$$

Isopropacetic acid.



$$\left\{\begin{matrix}\mathbf{C}\mathrm{Me_3}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. =$$

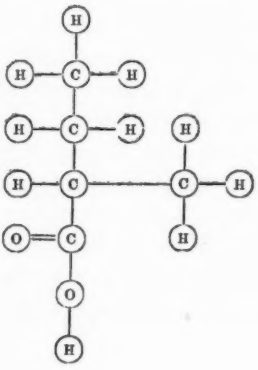
Trimethacetic acid.



One other acid not yet obtained would complete this isomeric group, and would be produced by the substitution of two atoms of hydrogen in the methyl of acetic acid, the one by ethyl and the other by methyl. This acid, which might be appropriately named ethomethacetic acid, would have the following constitutional formula :—

$$\left\{\begin{matrix}\mathbf{C}\mathrm{EtMeH}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right. =$$

Ethomethacetic acid.



In normal butyric and propionic acids we see the first step in the formation of this missing acid realised, and the introduction of methyl into the first, or of ethyl into the second, in the place of one of the remaining atoms of original methylic hydrogen, would infallibly give rise to the acid in question.

It will be observed on inspecting the above formulæ, that both valeric and isopropacetic acids are normal acids, that is they both contain two atoms of undisplaced methylic hydrogen. The missing ethomethacetic acid would be a secondary acid, because it would contain only one atom of undisplaced methylic hydrogen, whilst trimethacetic acid is a tertiary acid, containing no undisplaced methylic hydrogen.

The remarkable circumstance that both valeric and isopropacetic acid are normal acids, led us to expect a very close resemblance between them, and this anticipation has been completely verified by a rigid comparison of the properties of the two bodies. In odour, taste, and general appearance they are quite undistinguishable from each other, and the following table of comparison reveals no tangible difference between them :—

	Isopropacetic Acid.	Valeric Acid.
Sp. gravity of liquid at 0° C.	·95357	·9555 (H. Kopp)
Boiling point	175° C.	175° C.
Specific gravity of ether at 18° C.	·87166	·866
Boiling point of ether	134°—135° C.	133·5° C.
Silver-salt	Nacreous scales	Nacreous scales
Solubility of silver-salt in water at 10° C.	100 parts of water dissolve ·187 part	100 parts of water dissolve ·180 part

Had these acids been examined a few years ago, no chemist would have hesitated to pronounce them identical on the foregoing evidence, but the present state of our knowledge regarding the constitution of carbon compounds renders such an opinion utterly untenable. Nevertheless we were unwilling to leave the evidence of their difference upon a theoretical basis only, and we have had the satisfaction of discovering a sharply defined physical difference between them. This difference is exhibited in their behaviour towards circularly polarised light. The synthesized acid is inactive, whilst valeric acid, prepared

from amylic alcohol, powerfully rotates the plane of polarization to the right. We have also ascertained that the same difference extends to their respective ethers. Professor Wanklyn has kindly titrated the ethylic valerate used for this experiment, and has proved it to be of a purity almost absolute, and free from amylic alcohol, which moreover rotates the plane of polarization to the left. Two experiments gave 30·17 parts and 30·15 parts as the amount of potassium necessary to displace the ethyl in 100 parts of this valeric ether. Theory requires 30·08 parts. Wurtz* states that valeric acid is inactive towards the polarized ray, whilst we find that this acid possesses a tolerably powerful right-handed rotation. Our valeric acid was prepared from a sample of amylic alcohol, which possessed a left-handed rotation. Pasteur has shown† that ordinary amylic alcohol contains two varieties capable of being separated from each other; one of these is inactive, whilst a stratum of the other, 50 centimetres thick, exhibits a left-handed rotation of 20°. It is highly probable that the active amylic alcohol gives active valeric acid, and the inactive alcohol an inactive acid, in which case the inactivity of Wurtz's sample of valeric acid would be explained on the supposition that it was prepared from a sample of amylic alcohol, containing only the inactive variety. We are at present engaged in the elucidation of this question, with the view of ascertaining more especially whether or not the inactive amylic alcohol contains isopropyl, and therefore possesses the constitutional formula

$$\left\{\begin{matrix}\mathbf{C}\beta\mathrm{PrH_2}\\ \mathbf{C}\mathrm{H_2Ho}\end{matrix}\right.$$

* Ann. Ch. Phys., xliv, 275.

† Compt. rend., xli, 296, and Ann. Ch. Pharm., xcvi, 255.

VII.—*On the Alloys of Magnesium.*

By James Parkinson.

Magnesium, when heated to redness, has a most powerful affinity for oxygen, and in order to alloy this metal with others, it is necessary to avoid bringing substances containing oxygen into contact with it. The fluxes used must therefore be free from oxygen, and in order to prevent the reduction of silicium from free and combined silica, and the loss of magnesium by volatilization, it is necessary to avoid heating the fused mass too long.

Easily fusible metals such as tin, bismuth, cadmium, lead, zinc, and antimony, may be fused in small quantity with an equal bulk or less, of magnesium, *in an atmosphere of hydrogen*, in a hard German glass test-tube over the coal-gas flame of a good air-burner.

Fig. 1.

The less fusible metals are, with the exception of silver, gold, and copper, with difficulty alloyed in a flux, or in brasqued crucibles; but silver, gold, and copper may be fused and alloyed either in a flux composed of equal parts of fluor spar and cryolite, or of fluor spar and common salt—and with the exception of zinc and cadmium—the easily fusible metals may be fused in like manner.

The flux should be fused in a stout Cornish crucible before the metal is added, and the magnesium secured to an iron rod by a piece of clean iron wire, as shown in Fig. 1, in order to keep it under the surface of the flux. An iron rod about one-quarter of an inch diameter and three feet long is well suited for this purpose, bent and

twisted at one end into the shape of a letter O, of about one inch diameter, in the manner shown. The small piece of iron wire should be tightly wound round the piece of magnesium in one coil, then the two ends twisted spirally for about half an inch to an inch (equal to the depth of the flux in which the metals are to be alloyed), and the remaining length wound round the iron rod tightly, so as to secure the magnesium with as little wire as possible, so that, should the end of the rod be required to press down the magnesium, the temperature of the flux may not be too greatly reduced on plunging it into the fused mass. In the event of the displacement of the magnesium, the bent end of the rod enables the operator to keep it under, and thereby prevent loss by spirting and oxidation.

Magnesium being highly volatile at high temperatures, and very light, and consequently occupying a large space, it considerably diminishes the temperature of the fused mass when first plunged into it, so that the flux thickens and adheres to the rod, but in a few seconds the temperature rises, and it becomes again tranquil and liquid; the rod may then be removed without contaminating the alloy with iron, and without any adhering metal. The rod is readily cleaned by a few taps of a hammer both before and after cooling it in water. There is always a loss of magnesium by volatilization, if the heat be continued after the fusion and after the metals are alloyed. The alloy should therefore be removed as soon as possible and quickly cooled, either by pouring out into an ingot-mould, or by cooling the crucible in water, taking care not to let any water come in contact with the alloy, otherwise a strong galvanic action will in most cases be set up, and the button will become much corroded. Flashes of light, due to the oxidation of the magnesium, are emitted with all magnesium-alloys on passage of the metal from the crucible to the ingot-mould. The magnesium may be oxidised out of some (if not all) of these alloys, simply by fusion with a flux of carbonate of soda and carbon. With the exception of some of the alloys of tin, silver, and lead with magnesium in notable quantity, the colour of the *white* metals is not materially altered, but the physical properties are remarkably changed; and, without exception, the magnesium renders all alloys very brittle; even "triple alloys" of magnesium with gold and silver, and also with nickel and copper, are most remarkably brittle. The fracture is more or less crys-

talline, and the hardness is slightly increased above that of magnesium, or that of the metal or metals with which it is alloyed. Exposed to the action of the atmosphere, they tarnish more or less rapidly; those alloys with mercury, bismuth, lead, phosphorus, and also arsenic, are very rapidly tarnished, and decompose water most readily. None of these alloys of magnesium promise to be of any *practical* importance in the arts, but the powerful deoxidizing properties of magnesium may ultimately be found useful.

In employing *brasqued crucibles*, much time and trouble are required to arrange the metals and plug, lute, and pack tightly, so as to exclude the air, and prevent oxidation.

With *equal parts* of fluor-spar and cryolite as a flux, a fusion may be readily effected in a stout Cornish crucible, and with more satisfactory results where applicable. When cryolite cannot be had, a mixture of $\frac{1}{3}$rd fluor-spar and $\frac{2}{3}$rds common salt will answer most purposes, more especially for copper, silver, and gold. The alloys should be cleaned, without brushing them, in water, or else the surface will rapidly tarnish, and alloys of tin, bismuth, lead, and antimony will even set up a slow oxidation throughout, so that the fresh fracture will, in a very short time, become dull and coated with an oxide. It is remarkable that the alloy of tin and magnesium prepared in a flux of fluor-spar and common salt has the *grey colour* and lustre of steel, and a *fine granular* fracture, which soon becomes dull and coated with a greyish oxide on exposure to the air; while the same alloy, *prepared by fusing the metals together in an atmosphere of hydrogen*, or *in a brasqued crucible* with more than 2 per cent. of magnesium, tarnishes less when exposed to the air, and has a *lavender-tinted* fracture and prismatic crystalline structure, but when polished, a steel-grey colour and lustre.

The results of alloys prepared by heating the metals together in *hydrogen*, and also in the following fluxes, may be briefly summed up in a tabular form *in the order of the fusibility of the metals* with which magnesium alloys:—

TABLE I.—ALLOYS OF MAGNESIUM *prepared in an atmosphere of pure dry Hydrogen, in a hard German glass test-tube, over the Gas-flame of a good Air-burner.*

Metals.	Nature of Combination.	Lustre and Colour.	Hardness and Tenacity.	Fracture.	Remarks.
Mercury with 1 per cent. to 7 per cent. magnesium.	Combination begins below boiling point of mercury without combustion, and without corrosion of tube.	Silver-white colour; highly lustrous. The lustre not permanent.	With the 7 per cent. magnesium, soft and brittle; easily crumbled between the fingers.	Finely granular; white fracture.	Oxidized rapidly in the air, and also by water. The oxidized amalgam is a brownish black powder.
Sodium with magnesium.	Combination begins without combustion at a dull red heat, and corrodes and blackens tube.	Silver-white colour and lustre.	Soft and rather brittle.	Finely granular.	Water is rapidly decomposed by it. The sodium oxidizes and is dissolved by the water, and magnesium separates in small globules nearly free from sodium.
Tin with 2 per cent. to 10 per cent. magnesium.	Combination takes place at a dull red heat.	Steel-grey lustre, which tarnishes rapidly.	Harder than tin, but softer than magnesium, and far more brittle.	With more than 2 per cent. magnesium gives a lavender-tinted prismatic crystalline fracture.	The alloy prepared in brasqued crucible also has a lavender tint, but when re-fused in fluor-spar and common salt it gives a steel-grey colour. (See Table II.)
Cadmium with 10 per cent. magnesium.	Combination begins at a dull red heat, and the mass boils, if the heat is increased suddenly to redness.	Silver-white colour, and brilliant lustre.	About as brittle and as hard as magnesium.	Coarsely crystalline, and highly lustrous.	Tarnishes slowly. Within a period of six months it broke up into small tarnished fragments, though kept loosely corked in a tube.

Bismuth with 10 per cent. magnesium.	Energetic combination and vivid combustion at a red heat.	When polished, steel-grey lustre and colour. Crystals laminated, and colour of specular iron ore.	Very soft and brittle; easily crumbled between the fingers.	Coarsely crystalline; laminated; submetallic and lustrous.	Oxidizes and deliquesces in the air very rapidly, readily decomposes water, and partly dissolved by water.
Lead with 10 per cent. magnesium	Combination takes place at a dull red heat; tube blackened.	Very brittle. Steel-grey colour, and lustre when polished.	About as hard as zinc, and very brittle.	Finely granular, and lavender-tinted fracture. Like tin and magnesium alloy.	Fresh fracture becomes suddenly dull, and coated with a black oxide. Exposed to the air disintegrates and gives a black oxide, mixed with some metal.
Zinc with 10 per cent. magnesium	Combination takes place at a red heat, tube blackened.	Tin-white colour, and highly lustrous.	Very hard and very brittle. Some with 20 per cent. magnesium.	Smooth fracture, and highly lustrous.	This alloy appears to tarnish the least of any alloy of magnesium. Next to this the alloy of copper and magnesium tarnishes least.
Antimony with 10 per cent. magnesium.	Combination takes place at a much higher degree of heat than any of the above metals.	Steel-grey colour, and lustre.	Harder than antimony and equally brittle.	Dull lustre, and finely granular.	Decomposes water, and rapidly oxidizes in the air.
Silver with 10 per cent. magnesium	Combination takes place at a red heat, about the fusing point of Ag.	When polished, silver-white colour and lustre; tarnishes yellow.	Harder than magnesium and about as brittle.	Deep straw-yellow, and finely granular. Coarsely granular, with 20 per cent. magnesium.	Yellowish fracture, with 10 per cent. magnesium, whether prepared in hydrogen, in a brasqued crucible, or in a flux of fluor-spar and cryolite, but a bluish-white colour with 20 per cent. magnesium.
Platinum with magnesium.	Combination begins at a red heat, with vivid combustion.	Tin-white colour, and lustre.	White colour.	Finely granular.	Partly soluble in hydrochloric acid.

TABLE II.—ALLOYS OF MAGNESIUM *with the easily fusible Metals prepared in a flux of 2 parts Chloride of Sodium and 1 part Fluor-spar (free from Zinc or Lead).*

Metals.	Time and Degree of Heat of Fusion on plunging magnesium into the Fusion.	Lustre and Colour.	Hardness and Tenacity.	Fracture.	Remarks.
Tin with 10 per cent. magnesium	450 grs. tin with 50 grs. magnesium were fused and alloyed at a dull red heat, in five minutes, with 3 per cent. loss.	Steel-grey colour and lustre.	Very brittle; harder than tin, but softer than magnesium and far more brittle.	Finely granular; steel-grey colour and lustre, but not the least like that prepared in hydrogen or in brasqued crucible.	Tin liquates through the fracture of slag while cooling. Sp. gr. 5·2; decomposed water slowly.
Bismuth with 10 per cent. magnesium	450 grs. bismuth with 50 grs. magnesium gave also a tranquil fusion, and alloyed in about five minutes at a dull red heat; a large loss and dark-coloured slag.	Colour and lustre that of bismuth, but more brittle; instantly tarnishes in the air.	Very brittle; softer than bismuth and crumbles under the blow of a hammer.	Coarsely crystalline and laminated: resembles micaceous specular iron ore.	Deliquesces when exposed to the air, and immediately becomes dull on the fresh fractured surface. The action of the air and moisture is so great that it hisses distinctly when held in the hand.
Lead with 10 per cent. magnesium	Fused and alloyed in about three minutes at a dull red heat. Tranquil fusion and 6 per cent. loss.	Steel-grey colour and lustre: soon blackens in the air, then whitens, and in a few weeks breaks up.	Harder than magnesium and exceedingly brittle. Very brittle even with 4 per cent. magnesium.	Finely granular with steel-grey colour, and quickly blackens in the air.	The crust of oxide formed is thick and greyish white, and gives dull fracture when ingot is broken up after surface has oxidized.
Zinc with magnesium	Failed to obtain an alloy at a dull red heat in three experiments. The reaction was violent and explosive in each experiment. Obtained an alloy by heating the metals together in an atmosphere of hydrogen. See Table I.				
Antimony with 10 per cent. magnesium.	Combination took place at a red heat, with about 6 per cent. loss.	Steel-grey colour and lustre.	Very brittle, and about as hard as magnesium.	Coarsely crystalline; finely granular; resembles antimonite.	Decomposes water rapidly, and like the alloy bismuth and magnesium gives a strong galvanic action when breathed upon, and tarnishes immediately.

TABLE III.—ALLOYS OF MAGNESIUM *with the less fusible Metals prepared in a flux of Fluor-spar and Cryolite (Silver with Magnesium, and Copper with Magnesium, fused in equal parts of Fluor-spar and Common Salt).*

Metals.	* Time and Degree of Heat of Fusion.	Lustre and Colour.	Hardness and Tenacity.	Fracture.	Remarks.
Aluminum with magnesium.	Failed to obtain an alloy of aluminum and magnesium. The product was found on analysis to contain aluminum and silicium (about 25 per cent. Si). The fusion was about five minutes in one, and nearly ten minutes in another experiment. The product weighed less than the amount of aluminum taken in both experiments. Obtained an alloy of aluminum and magnesium in a crucible brasqued with fresh and pure calcined magnesia.				
Silver with 10 per cent. magnesium	200 grs. silver fused and alloyed in about four minutes at a red heat, inclusive of time occupied to fuse 50 grs. of magnesium.	Bluish-white colour, with 20 per cent. magnesium, and yellowish-white. with 10 per cent. magnesium.	Harder than magnesium.	Coarsely crystalline and bluish-white, like zinc, with 20 per cent., but finely granular and yellowish with 10 per cent. magnesium.	Tarnishes slowly.
Copper with magnesium	200 grs. copper fused and alloyed with 50 magnesium in about seven minutes at a bright red heat. Loss 1¾ per cent.	Reddish-yellow, or yellowish, or golden colour, according to percentage of magnesium.	Very brittle; 1 per cent. magnesium renders the copper brittle; and with 15 per cent. the alloy may be powdered in an iron mortar.	Smooth vitreous fracture, and tarnishes only slowly.	With 15 per cent. magnesium the alloy has a sp. gr. 5·95, and nearly as brittle as glass.
Gold with magnesium	Time of fusion about 15 minutes, at a bright red heat.	Golden colour and lustre.	Hard and brittle.	Finely granular, some specks of white metal, as if the magnesium was not chemically intermixed.	

* The metals were not added until the flux was thoroughly fused and tranquil: the metal with which the magnesium was alloyed was fused before plunging the magnesium into the melted mass.

TABLE III—*continued.*

Iron with magnesium.	Failed to obtain an alloy iron and magnesium. Fused 167 grs. wrought iron in the state of fine wire (coiled up) in about 1¼ hour, then plunged a lump of magnesium into the fused metal. The button, however, contained only a *trace* of magnesium, and its physical character remained unchanged in one experiment only.
Cobalt with magnesium.	Failed to obtain an alloy cobalt and magnesium; first fusing cobalt, then plunging magnesium into it in like manner, but no magnesium was present in the button.
Nickel with magnesium.	Failed to obtain an alloy nickel and magnesium by fusing the metals together in brasqued crucible, a trace only of magnesium being found present on analysis of button.

TABLE IV.—TRIPLE ALLOYS OF MAGNESIUM, *prepared by fusing in equal parts of Fluor-spar and Common Salt.*

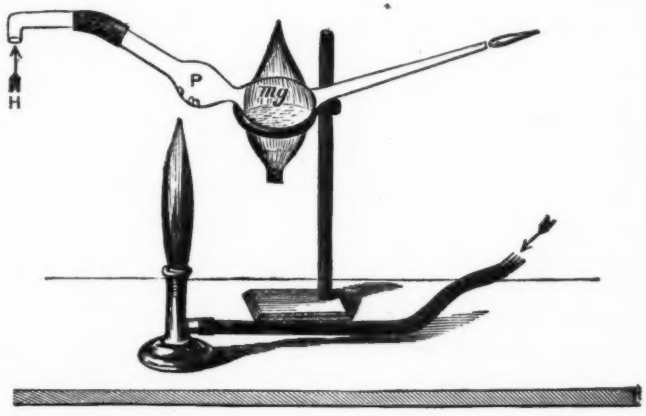
Metals.	Colour and Lustre.	Hardness and Tenacity.	Fracture.	Remarks.
Bismuth with copper and magnesium.	Brass-yellow polish; soon becomes dull.	Very brittle, and about as hard as copper coin.	Dull and granular fracture, with specks of white metal intermixed.	Bismuth liquates out, and coats surface of button with a thin coating while cooling.
Gold with Copper and magnesium.	Steel-grey colour tinted yellow.	Very hard, and very brittle.	Coarsely crystalline with steel-grey colour.	When freshly fractured, resembles the finest specimens of white cast iron.
Nickel with Copper and 6 per cent. magnesium.	Silver-white colour, and high lustre.	Exceedingly brittle, and very hard.	Finely granular and silver-white.	Composed of copper, 65·63; nickel, 28·24; magnesium, 6·34.

Behaviour of Magnesium with Non-metallic Elements.

Magnesium combines very energetically at high temperatures with *phosphorus*, *arsenic*, and *sulphur*, with which it forms remarkably unstable compounds. The coherent and difficultly fusible alloys of magnesium with phosphorus and with arsenic, oxidise rapidly, and fall to powder when exposed for a short time only to the air at common temperatures, the alloy of sulphide of magnesium only slowly.

The apparatus used for the experiments with phosphorus and arsenic was made from a stout half-inch diameter glass tube, of difficultly fusible glass, such as is used in organic analysis. The two ends of a piece of a combustion-tube (eight inches long) were drawn out to about a quarter of an inch in diameter and four or five inches long, and the middle part blown out into two bulbs of about three-quarters of an inch in diameter (Fig. 2). The two ends were bent upwards, at an angle of about 30 degrees, and the larger orifice of one of the ends was connected to a

Fig. 2.



hydrogen apparatus by an india-rubber connecter, after placing the substances in the bulbs; and then, after displacing the atmospheric air in the tube by a rapid and dry current of hydrogen, the bulbs were heated by means of the gas flame of two or more good air-burners. The current of hydrogen was con-

tinued after withdrawing the flame of the burners until cold, and the product was weighed immediately.

Phosphorus and Magnesium.

Pieces of phosphorus were placed in one bulb and magnesium filings in the other. The experiment was conducted as above described, and the melted phosphorus was allowed to flow slowly, by inclining the tube over the magnesium filings heated to dull redness. Then the flame of another burner was used, with a view of maintaining uniformity of temperature, and for volatilizing the excess of phosphorus from the tube. The combustion which took place at a dull red heat was highly luminous and vivid, and the tube was corroded and fractured in several cases from the sudden increase of heat during combustion. With 3 grs. magnesium filings the increased weight was in the first experiment 2·45 grs., in the second 1·98 grs., and in the third 2·08 grs. The product is a hard, brittle, coherent, semi-metallic and difficultly fusible mass, of a dark-brown colour, with a fibrous crystalline fracture; it is immediately tarnished on exposure to the air, and within a few hours falls to a flocculent powder, at the same time undergoing several changes of colour. It first becomes brownish-black, then brown, yellowish, straw-yellow, and finally yields a permanent greyish-white powder, emitting non-inflammable phosphoretted hydrogen during its oxidation, as well as when thrown into water, or into dilute hydrochloric acid. The freshly oxidized product, when heated to dull redness, in an open tube, undergoes combustion, and becomes whiter in colour. It is completely dissolved by dilute hydrochloric acid.

A paper on phosphide of magnesium, by Mr. Blunt, is published in the Chemical Journal for 1865 [2] iii, 106, the results of which do not coincide with the above. The *black powder*, said to be a phosphide of magnesium, and described as a very stable compound, is probably carbon, mixed with some phosphide of magnesium, the carbon to which it owes its blackness being probably deposited by the reaction of magnesium upon the carbonic acid used in the experiment. In all cases magnesium decomposes the glass in which the experiments are conducted, and is stained black by the reduction of the silicium of the glass, with which it combines and forms a silicide. Oxygen

is also liberated at the same time, which combines with the magnesium, and probably with the phosphorus also. See the reaction of magnesium upon carbonic acid, and also upon carbonates further on.

Sulphur and Magnesium.

In combining sulphur with magnesium, a single bulb-tube, constructed as before described, was connected with a small flask containing sulphur used for generating sulphur-vapour; the magnesium filings, mixed with a little sulphur, gave better results than sulphur-vapour alone. The heat was slowly raised to dull redness by means of the gas-flame of a good air burner. The product was a brownish-black, scoriaceous, coherent coke-like mass, hard and brittle, and mixed with a little oxide of magnesium, and some undecomposed filings. On exposure for some time to the air, the difficultly fusible sulphide slowly tarnishes, and evolves sulphuretted hydrogen, and the finely granular and bright steel-grey fracture becomes dull and coated with a greyish oxide; it is partly soluble, with straw-yellow coloration in water, with evolution of sulphide of hydrogen, but on exposure to light, it deposits sulphur and becomes colourless.

Arsenic and Magnesium.

The single bulb-tube was connected with a hydrogen apparatus, through which a rapid current of pure dry hydrogen was passed; and when all the atmospheric air was displaced thereby, the magnesium filings, mixed with arsenic, placed in the bulb part, were heated slowly to redness. In one experiment, 3 grs. magnesium filings, mixed with 15 grs. arsenic, gave violent and vivid combustion, with evolution of much heat. The heat was continued until the hydrogen flame at the orifice of tube ceased to be luminous; the current of hydrogen was passed through until the ignition tube was cold, and then the product was immediately weighed. The loss was found to be 8·8 grs., showing that about 6·2 grs. arsenic were fixed and combined with 3 grs. magnesium. 3 grs. magnesium heated in like manner for ten minutes, lost only 0·05 grs., hence the 8·8 grs. lost were almost entirely due to the volatilization of arsenic. The product was a hard, brittle, and difficultly fusible mass, of a choco-

late-brown colour and dull lustre, with finely grained fracture, and a brown sub-metallic lustre; it crumbled up, in a few hours, into a dark-brown powder.

The same quantity of magnesium filings and arsenic, suddenly heated in a glass test-tube over the flame of a good air-burner, gave a vivid and violent action, slightly explosive. Another experiment with 3 grs. magnesium and 20 grs. arsenic gave an explosion with loud report, and shattered the bottom of the test-tube into fine fragments.

Behaviour of Magnesium with Oxides and Carbonates.

The de-oxidizing action of magnesium at high temperatures is less violent than its combination with the non-metallic elements, but sufficient to give a vivid combustion, which occurs at a slightly higher temperature.

Pure lime is decomposed at a red heat by magnesium filings, with only a slow and dull combustion, and yields a straw-yellow powder, which has a fetid smell, and decomposes water slowly.

Pure alumina, heated to redness with magnesium filings gives a vivid combustion, and a blackish-brown powder, which rapidly decomposes water and gives a violent action with moderate dilute hydrochloric acid, sufficient in one experiment to ignite the hydrogen evolved in the reaction.

Sesquioxide of chromium, heated to redness with magnesium-filings, gives a vivid combustion and a *black* powder, which decomposes water. The inside of a glass tube, in which some small fragments of magnesium were heated with chromic oxide, was coated with a thin white metallic coat, which, when washed and scraped clean, gave a silver-white lustre, and on ignition in the air burnt with evolution of much light and gave a greenish-yellow oxide—indicating the reduction of the oxide to the metallic state—and combined with the magnesium, and, probably, also with silicium derived from the tube.

Titanic acid, heated to redness with magnesium-filings, gives a vivid combustion and a bluish-black, gritty powder, partly, if not wholly, insoluble in cold dilute hydrochloric acid, which, when dried and heated in the open tube, burns like tinder, and when thrown into the flame emits bright-red scintillations.

Magnesia (pure and free from carbonic acid), heated with magnesium-filings at a red heat, is not acted upon, but the carbonate gives a slow combustion, with deposition of carbon and a *brownish-black* powder; so also do other carbonates.

Silica, heated to redness with magnesium-filings, gives a vivid reaction, and a brown to bluish-black powder according to the degree of heat and vividness of reaction; if the silicium is in excess, and the combustion slow, the product is *brown;* but, if the magnesium is in excess, and the combustion vivid, the *product* is a *black, gritty powder;* which, in the latter case, gives a much stronger reaction when thrown into hydrochloric acid, and evolves more silicide of hydrogen and with louder detonation as the gas spontaneously ignites in the air—hence a "silicide of magnesium" is formed in greater quantity in one case than in the other. The *black powder* contains the most silicide. The lighter coloured product probably contains more of anhydrous silicate of magnesia. 1 part magnesium-filings to 2 parts silica, heated in a current of hydrogen (in fine powder), give a *brown* gritty powder. *Equal parts* magnesium and silica give a more cemented and *brownish-black* powder; and with 3 parts magnesium and 1 part of silica the product was a *bluish-black powder* with sub-metallic lustre, hard and brittle. When the darkest coloured products are thrown into concentrated sulphuric acid, no spontaneously inflammable gas is evolved until the substance is rubbed with a glass rod against the sides of the tube, and then no detonation takes place, but luminosity only is emitted. *Similar results* are obtained, when the blackened part of the glass tube in which magnesium has been heated, either alone or with other substances, is broken up into fine fragments and thrown into either dilute or strong hydrochloric acid, evidencing the presence of *silicide of magnesium* from the reaction of magnesium upon the glass. The same powerful deoxidization and production of silicide of magnesium takes place also with silicates when heated to redness with magnesium.

Behaviour of Magnesium with Oxides of Carbon.

Carbonic oxide and *carbonic acid*, like the carbonates, are decomposed when heated to redness with magnesium-filings. The magnesium is oxidised and the carbon is deposited in admixture

with the oxide, so that the product resembles lamp-black. The combustion is vivid and highly luminous.

Behaviour of Magnesium with Carbides of Hydrogen.

1. *With Coal-gas.*—Whether or not the coal-gas be washed and dried before heating with magnesium-filings, a slow combustion takes place, and the product resembles that obtained by heating magnesium in carbonic acid, but with this difference, that it decomposes water slowly, with evolution of fetid hydrogen, while the product formed by heating magnesium with carbonic acid, does not decompose water.

2 grs. magnesium-filings, heated to redness in a bulb-ignition tube in a current of coal-gas, unwashed, absorbed 1·67 gr. carbon and oxygen.

When 3 grs. magnesium-filings were heated to redness in a current of coal-gas, washed by passing it through milk of lime, ferric hydrate, and acetate of lead, and dried with oil of vitriol, the increase of weight by ignition in like manner was only 1·43 gr. Marsh-gas was found to have little or no effect on magnesium-filings, hence it would appear that the combustion in these experiments was due to the carbonic oxide; and probably, also, to the benzol present in the coal-gas.

2. *With Marsh-gas.*—This gas generated from a mixture of acetate of soda, quick-lime and caustic potash, was washed and dried by passing it through oil of vitriol, and, after expelling all the air in the apparatus and tube, 3 grains of magnesium-filings were heated in it, as before, to redness for five or ten minutes, then cooled and weighed. The increase of weight was only 0·03 gr.; the filings were merely tarnished, and a little carbon deposited, derived probably from carbonic acid not absorbed by the lime and potash. Another experiment, also with 3 grs. magnesium-filings, heated to a *higher* temperature for ten or twelve minutes, gave an increase in weight of 0·08 gr. The filings were only slightly tarnished as in the first experiment.

3. *With Benzol.*—3 grs. magnesium-filings heated in pure benzol-vapour, gave no combustion, but the filings were rendered very brittle, and coloured black, and decomposed water. On dissolving them in dilute hydrochloric acid a separation of carbon took place. The increase of weight was 0·73 gr.

Sulphurous acid (SO_2) prepared from copper and sulphuric acid, washed with concentrated sulphuric acid, and passed over magnesium-filings heated to redness in a bulb ignition-tube by the gas flame of a good air-burner, gave a vivid luminous combustion. Sulphur condensed on the cool part of the tube, which was expelled by aid of another flame. The current of dry sulphurous acid was passed through the ignition-tube for some time after, withdrawing the flame until the tube was cold, when the product was removed and re-weighed. The combustion of 3 grains magnesium-filings (after expelling all the sulphur from the tube) gave a product which weighed 4·86 grs., and when treated with nitric acid, evolved fumes of nitrous acid, and gave with chloride of barium a precipitate insoluble in hydrochloric acid, thus showing that the sulphurous acid was not completely reduced.

Before closing this paper it is desirable to draw attention to the erroneous statements on alloys of magnesium which have gone uncontradicted up to the present time. It has been said that magnesium would give a somewhat tenacious and malleable and useful alloy with copper. It is, however, much to be regretted that none of the alloys of magnesium and copper possess the least tenacity or malleability. Magnesium alloys with copper as with most (if not all) metals in different proportions, and the larger the proportion of magnesium, the more brittle is the alloy. With copper the colour becomes paler, according to the increased proportion of magnesium.

VIII.—*On the Oxidation of Ethylic and Methylic Benzoates.*

By R. H. Smith, F.C.S.

At the suggestion of Mr. Chapman, I was induced to undertake the following investigation:—

Pure ethylic benzoate was digested with excess of a 12 per cent. solution of potassic dichromate and dilute sulphuric acid, at the temperature of 100° C. for 9 or 10 hours. The tube was then removed from the water-bath and left to stand all night. In the morning beautiful white crystals were observed, and the tube on opening gave little or no carbonic acid, but there was a strong smell of acetic acid. The white crystals thus produced were dissolved in a large quantity of hot water, and a solution of argentic nitrate added. The whole was then heated and set aside to crystallise. After another crystallisation the salt was submitted to analysis.

0·1355 grm. of the silver-salt was precipitated with hydrochloric acid, and the resulting argentic chloride washed, dried, and ignited. The argentic chloride weighed 0·085 grm., whence the percentage of silver is 47·15, agreeing closely with the theoretical percentage of silver in argentic benzoate—

$C_7H_5AgO_2$, which is 47·16.

The liquid also found in the tube was carefully distilled, until it no longer retained sulphuric acid. A portion of this was heated with alcohol and sulphuric acid, when the well known smell of ethylic acetate was obtained. The remaining portion was then treated with baric carbonate, which dissolved freely; an excess was added, and the liquid boiled and filtered. The resulting clear solution was evaporated to dryness in the water-bath, and the residue dried at 110° C.

I. 0·0970 grm. of the barium-salt was precipitated with dilute sulphuric acid, and the baric sulphate ignited. It weighed 0·0885 grm. Percentage of barium, 53·60.

II. 0·1140 grm. gave 0·1040 grm. of baric sulphate. Percentage of barium, 53·59.

These numbers agree very nearly with the theoretical percentage of barium in baric acetate $Ba''(C_2H_3O_2)_2$, viz., 53·72.

In one experiment, the carbonic acid was determined with the following result :—

1·7990 grm. of ethylic benzoate gave 0·0020 grm. of carbonic acid. This is only a trace. It is quite possible therefore to produce benzoic and acetic acids from ethylic benzoate, without carbonic acid, a result which is in harmony with theory.

$$\left.\begin{matrix}C_7H_5\\C_2H_5\end{matrix}\right\}O_2 + O_2 = \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}C_7H_5\\H\end{matrix}\right\}O_2.$$

After having tried the action of potassic dichromate of ethylic benzoate, I was induced to try it on the methyl-compound.

Methylic benzoate is decomposed by potassic dichromate in a similar manner. A quantity of this compound (prepared by the distillation of benzoic acid with wood-spirit and sulphuric acid) was introduced into a tube with an 8 % solution of the potassic dichromate, and the tube, after being sealed, was digested in the water-bath for several hours. It was then allowed to cool, when the benzoic acid made its appearance, entirely filling the tube with white crystals. On opening the tube, carbonic acid escaped; the contents of the tube were thrown upon a filter, by which most of the benzoic acid was separated from the liquid. The liquid was then distilled, the distillate converted into barium salt, and the barium determined, which gave a percentage agreeing very closely to that required by formate of barium. The benzoic acid was converted into the silver-salt, and the percentage of silver determined, which also agreed with that required by argentic benzoate.

Methylic benzoate is therefore resolved, as might be expected, into benzoic acid, carbonic acid, and more or less formic acid.

It will be seen from the foregoing results, that benzoic acid, and probably the acids of the benzoic series, will resist the power of oxidising agents, as well as those of the acetic series, as shown by Messrs. Chapman and Thorp.

These experiments were performed in the laboratory of the East London Soap Works.

IX.—*On a new Synthesis of Formic Acid.*

By Ernest Theophron Chapman.

[Contribution from the Laboratory of the London Institution.]

From a careful consideration of the results obtained by Mr. Thorp and myself in our investigation of the action of

oxidizing agents on organic bodies, it appeared to me difficult to account for many of the reactions, on the assumption that nascent oxygen was the sole agent in effecting the change. Thus, to take a very simple case, acetate of ethyl yields by oxidation two equivalents of acetic acid. In this case we have the same amount of hydrogen in the products obtained as in the substances operated upon. There are only two hypotheses possible in this case; either the ethyl has given up a portion of its hydrogen to the residue of the acetic acid, and has then itself appropriated two equivalents of oxygen, or the acetic ether has been decomposed by the assimilation of water and the substitution of oxygen for hydrogen, which amounts, in point of fact, to the action of hydroxyl. The assumption of the existence of hydroxyl in the oxidizing mixtures described in the paper before alluded to is, of course, an impossibility, for hydroxyl is immediately decomposed by these liquids. It is, we know, difficult to convert water into peroxide of hydrogen, but I am at a loss to understand the decomposition of bichromate of potash by concentrated sulphuric acid and heat, unless upon the assumption that hydroxyl is formed and at once decomposed by the excess of chromic acid present. This may appear a somewhat strained hypothesis. In order to give it weight, it was necessary to find some instance in which an unequivocal addition of hydrogen actually took place in such an oxidizing mixture. The following synthesis of formic acid furnishes such an instance; and I may remark that it was not undertaken with any idea of proving the truth of the foregoing hypothesis, though, had it not been for that hypothesis, I should, in all probability, neither have carried out the investigation, nor have put a correct interpretation on the results obtained.

I wished to know whether an acid solution of permanganate had any action upon carbon in the free state, *i.e.*, charcoal, lamp-black, &c. I found that it did act upon it, though but slowly, unless the solution were very concentrated and contained much acid. Still there was no question but that action, and very considerable action too, took place, provided sufficient time were allowed.

Crystallized permanganate of potash was dissolved in distilled water, and as much sulphuric acid added as would serve to liberate the permanganic acid. Lamp-black, which had been intensely ignited, was then added, and the mixture boiled,

After some hours' boiling, the solution had changed to a brownish-black colour. On standing it became clear. The colour of the clear liquid was then seen to be very faintly pink. A few drops more sulphuric acid were added, and the mixture distilled. The distillate was tasteless, or nearly so, and quite colourless, but, on adding a drop of ammonia and a little nitrate of silver, and boiling, a brown coloration was obtained. This constitutes the well-known test for formic acid. Now as even after the most intense ignition, lamp-black is said to retain traces of hydrogen—a statement which I am utterly unable to verify—I thought it advisable to employ some form of carbon which should be free from this objection. I tried passing carbonic acid over ignited sodium, but the yield of carbon from this experiment is deplorably small. The mixture of oxide of sodium and carbon was dissolved in distilled water.

[N.B.—The distilled water employed in this and all the following experiments had been re-distilled slowly from permanganate. The vessel in which the distillation was conducted, as well as the interior tube of the condenser and every other piece of glass apparatus used, had actually been made red-hot, so that it was free from all suspicion of organic matter. No cork, india-rubber, nor any form of organic matter was allowed to touch the interior of any of the vessels.]

The carbon gradually settled to the bottom, the alkaline solution above it was poured off, and the carbon washed by decantation with hot distilled water. It was then operated upon in the manner already described, very minute quantities of permanganate and sulphuric acid being employed. The operation was conducted in a digestion tube in the oil-bath. The tube was opened, a little sulphuric acid added, and a small portion of the liquid distilled off. But little of the carbon had disappeared. The liquid in the tube was poured off, more distilled water added, this again poured off, permanganate of potash and sulphuric acid again added, and the process repeated. This was done six times. The distillate obtained in this manner was rendered alkaline by a drop of solution of potash, evaporated down to a very small bulk, and the silver test for formic acid applied. It gave a very considerable precipitate.

The carbon used in the next experiments was obtained from bi-sulphide of carbon by the action of sodium. These two substances, when gently heated together, yield sulphide of sodium,

and a substance which I take to be pure carbon. It was washed in the manner previously described, and ignited in a covered platinum crucible. There was something more than a gramme of it. It was treated in precisely the same manner as the carbon obtained from carbonic acid had been, and the distillate obtained from it also gave the characteristic reaction with ammonio-nitrate of silver.

Still no quantity of formic acid had been collected. Reactions had been obtained which rendered it highly probable that formic acid was a product of the gradual oxidation of carbon, but the proof was still far from complete. The question in fact resolved itself into this apparently simpler one: where can we obtain pure carbon, not in the state of graphite, but in the amorphous condition? I believe that it may be obtained by simply igniting lamp black; but I fear most chemists would regard this as a delusion. I therefore mixed finely divided lamp-black with a small quantity of nitrate of potash, insufficient to burn more than half of it. This mixture was heated in a platinum crucible. It deflagrated. A portion of the carbon of course remained unconsumed. This carbon I hope may be regarded as free from organic matter; if not, I despair of finding any. The carbon was washed out of the accompanying potash-salts with distilled water and dilute sulphuric acid, and then treated in the manner previously described. By several operations nearly twenty grammes of it were obtained. These were divided amongst five digestion tubes; great care is necessary in these experiments in apportioning the acid to the permanganate. The solution must be perceptibly, but not more than perceptibly, alkaline at the close of the operation. If too much or too little acid is employed, no formic acid whatsoever is produced. This I have repeatedly verified to my cost. It is better that the liquid should be a little too alkaline than too acid. No advantage whatsoever is gained by using large quantities of permanganate. For instance, to four grammes of carbon, two decigrammes of permanganate of potash, and a corresponding quantity of sulphuric acid may be added apparently with exactly the same yield of formic acid as if only half the quantity were employed; in fact three of my tubes were always charged with about twice as much permanganate as the other two. The same number of operations were performed with each lot of carbon, viz., eight, and, as will be seen below, the amount of formic acid

obtained from the two tubes was almost exactly two-thirds of that obtained from the other three.

These operations extended over a considerable time—in fact, I was about six days engaged in charging these tubes and distilling from them. The product of two days' work was employed in obtaining satisfactory qualitative tests with oxide of mercury and ammonio-nitrate of silver. I obtained the reduction of both these substances.

The products of the other four days' work were devoted to analysis. About three-fifths of the total product (less than a decigramme) was employed in making a combustion, that is to say, the barium-salt obtained from the distillate was so employed. The remaining two-fifths, also converted into a barium-salt, were employed in determining the saturating capacity of the acid. Combustion was performed with chromate of lead. From the barium determination the following numbers were obtained :—

Substance taken.. 0·1402 Ba_2SO_4 found.. 0·1428
Therefore..... 59·89 % Ba.

By combustion the following numbers were obtained :—

Substance taken.. 0·2052 barium-salt.
Found ..... 0·0784 CO_2 and 0·0165 H_2O;
Therefore ..... 10·44 % C.,
and ·89 % H.

	Theory.	$CHBaO_2$.	Found
C	12	10·57	10·42
H	1	0·88	·89
Ba	68·5	60·35	59·89
O_2	32	28·20	—
	113·5	100·00	

It appears therefore beyond all doubt that formic acid may actually be obtained by the action of permanganic acid upon carbon. The process is difficult in the extreme, and little more than traces of the acid are obtained. It is only under the circumstances here specified that it is obtainable. We require free permanganic acid to act upon carbon, but a trace of potash or some alkali, and not more than a trace, must be present. I imagine that a comparatively large quantity of formic acid is formed and destroyed during the process.

X.—*On the Basicity of Tartaric Acid.*

By W. H. Perkin, F.R.S.

The tetratomic character of tartaric acid has been fully shown by its artificial formation from succinic acid. Reasoning upon this fact, several chemists have been induced to regard it also as tetrabasic, and, in confirmation of their hypothesis, have obtained several metallic combinations having the formula of tetrabasic tartrates. Thus Hugo Schiff found, that by heating the basic tartrate of lead to 130° C., it lost an equivalent of water, yielding a body which he regards as the tetrabasic lead-salt*, thus:—

$$C_4H_4Pb''_2O_6.Pb''_2O = H_2O + C_4H_2Pb''_2O_6.$$

Frisch also obtained a remarkable zinc-compound by boiling metallic zinc with potash and tartaric acid, and then carefully neutralising the solution with dilute nitric acid. The product has the composition

$$C_4H_2Zn''_2O_6 + \tfrac{1}{2}H_2O;$$

but if we consider the curious methods by which these substances have been produced, and the high temperatures at which some of them have been dried, and also the fact that tartaric acid will easily lose and again take up an equivalent of water, it becomes very difficult to judge of the true constitution of these bodies, especially as they are insoluble and cannot be crystallised. I have therefore thought it worth while to study the replaceable hydrogen in a different manner, and for this purpose have examined principally new derivatives obtained by the action of the chlorides of the acid radicals on tartaric ether.

Action of Chloride of Benzoyl on Tartaric and Paratartaric Ethers.

Chloride of benzoyl, when mixed with tartaric ether, does not react in the cold, but upon the application of heat hydrochloric

* Ann. Ch. Pharm., lxix, 272.

acid is abundantly given off. A mixture of these two bodies in about equivalent proportions (with, however, a slight excess of the ether), was heated in a water-bath for two or three hours. The product was well agitated at intervals with a solution of carbonate of sodium for the purpose of decomposing and removing any chloride of benzoyl or tartaric ether that might still be unacted upon. The alkaline solution was then separated from the new compound, which presented itself as a very viscid oil. This oil was then washed with water, dissolved in ether, and agitated with dry carbonate of sodium to remove any water or acid that might still be remaining. The ethereal solution was then filtered, and evaporated over the water-bath. By this means the new body was left as a very viscid but transparent oil. Two combustions of this substance in oxygen gave the following numbers:—

I.—·2270 of substance gave
·4799 of CO_2 and
·1205 of H_2O.
II.—·2315 of substance gave
·4913 of CO_2 and
·1217 of H_2O.

These numbers show the new product to be tartaric ether with one equivalent of hydrogen replaced by benzoyl:

$$(C_2H_5)_2.C_4H_3(C_7H_5O)O_6 = C_{15}H_{18}O_7,$$

as the following comparison will show:—

	Theory.		Experiment. I.	Experiment. II.
C_{15}	180	58·06	57·64	57·86
H_{18}	18	5·80	5·90	5·83
O_7	112	36·14	..	..
	310	100·00		

This product, after standing, especially under water, for two or three weeks, is almost entirely converted into a mass of colourless prismatic crystals, which, on being well pressed between bibulous paper under a very powerful screw-press, until perfectly free from oil, appears like a cake of white wax.

This, on being heated, easily fuses, and, on cooling, gradually solidifies into a beautifully radiated crystalline mass. A portion of this substance burnt in oxygen gave the following numbers:—

·2470 of substance, gave
·5256 of CO_2, and
·1330 of H_2O.

These furnish the following percentages:—

	Experiment.	Theory.
Carbon	58·03	58·06
Hydrogen	5·98	5·80

These numbers, it will be observed, correspond to those obtained on burning the non-crystalline product. When I first obtained this solid body, I was inclined to believe that it was isomeric with the oily product; but on further consideration I am induced to regard it simply as a purer substance, and this would appear to be the case from the analysis of the solid body yielding the best numbers. I have had an oily product standing for nearly three months, perfectly clear, but, on rubbing the sides of the bottle with a glass rod, it gradually began to crystallise.

This body I propose to call *benzotartaric ether*.

When pure, it is a white, inodorous solid, and may easily be powdered. It melts at 64° C., and cools to a viscid oil, which does not solidify until it has stood for some considerable time, but the introduction of a minute piece of the solid product immediately causes it to commence crystallising; and this takes place with a very considerable elevation of temperature. It crystallises in transparent prisms. If strongly heated, it distils with decomposition. It is soluble in all proportions in alcohol and ether; slightly soluble in boiling water, the solution becoming milky, and depositing oily drops on cooling; afterwards beautiful, but small prismatic crystals separate. Its aqueous solution has a slightly bitter taste. Its solutions do not change the colour of litmus paper. Aqueous potash appears to be without action upon it. With sodium it liberates hydrogen, and appears to form a sodium-compound. It is heavier than water.

Benzotartaric ether, when heated in a sealed tube to 100° C. with alcoholic ammonia, slowly decomposes and becomes of a

pale brownish-yellow colour. On evaporating the product to dryness, and then adding water, a few oily drops of the unchanged ether appear; these may be separated by filtering through wet paper. The filtrate, on the addition of hydrochloric acid, becomes filled with crystals of benzoic acid, and upon removing these and evaporating the solution to dryness, the residue presents a gummy appearance, and is very soluble in water. After boiling this with strong potash (which causes the evolution of a considerable quantity of ammonia), the addition of hydrochloric acid again causes a very large quantity of benzoic acid to separate, showing that in this reaction an amide is produced containing benzoyl; no *benzamide*, however, is formed. The products of this reaction are probably benzoic acid, tartramide, benzotartramide, and alcohol.

I have made several attempts to replace a second equivalent of hydrogen in tartaric ether by benzoyl, but at present have not succeeded. The result of heating tartaric ether with two equivalents of chloride of benzoyl, or of heating benzo-tartaric ether with one equivalent of the reagent, is the production of an oil the ethereal solution of which becomes gelatinous when evaporated. I have made several combustions of different preparations of this product, which were purified in various manners, the last one having been heated as high as 180° C. with the chloride of benzoyl. I have not, however, obtained any useful results. The carbon determinations gave numbers varying from 60·24 p. c. to 61, the hydrogen being about 5·4 p. c. This increase of carbon I do not think is due to the introduction of benzoyl, as even at a temperature as high as 240° C. a mixture of benzotartaric acid and chloride of benzoyl evolves scarcely any hydrochloric acid gas.

Chloride of benzoyl acts on paratartaric ether in precisely the same manner as upon tartaric ether, one equivalent of hydrogen being replaced. The product I propose to call *benzoparatartaric ether*, as it is isomeric, and not identical with the preceding body. It melts at a considerably lower temperature, viz., 57° C., and does not crystallise so easily as that substance.

Action of Alcoholic Potash on Benzotartaric Ether.

Benzotartaric ether is easily decomposed by alcoholic potash, yielding, if in excess, benzoic and tartaric acids; but the de-

composition may be moderated, and intermediate products obtained, if a dilute alcoholic solution of this ether and a weak solution of alcoholic potash are employed, the potash solution containing an insufficient quantity of alkali to decompose all the ether. A quantity of benzotartaric ether treated in this manner was gently heated until the excess of alcohol had evaporated; water was then added to cause the separation of any oily products. After filtration through a wet filter, the solution was acidified with hydrochloric acid; this caused the separation of an oil, which was again separated, and the clear liquid placed over sulphuric acid under the bell-jar of the air-pump. After evaporating in this manner for a few days, beautiful tufts of crystals separated, which, on being well washed with water, were found to be pure. A specimen dried at 100° C., and burnt in oxygen, gave the following numbers:—

·1474 of substance gave
·2964 of CO_2, and
·0675 of H_2O.

These numbers agree with the formula

$$\left.\begin{matrix} H \\ C_2H_5 \end{matrix}\right\} C_4H_3(C_7H_5O)O_6 = C_{13}H_{14}O_7,$$

as will be seen by the following comparison:—

	Theory.		Experiment.
C_{13}	156	55·32	54·84
H_{14}	14	4·96	5·08
O_7	112	39·72	..
	282	100·00	

This is therefore *ethylbenzotartaric acid*, or the benzotartrate of ethyl and hydrogen. This acid is a beautiful product, crystallising in tufts of hard needles, difficultly soluble in water, but excessively soluble in alcohol and ether. On evaporating its alcoholic or ethereal solution, it is deposited in fan-shaped masses of crystals. Its aqueous solution reddens litmus paper. It is easily decomposed by potash, and its salts appear to be rather unstable. Owing to the small quantity I have obtained of this acid, I have been unable to examine it more fully.

The mother-liquors from ethylbenzotartaric acid contain con-

siderable quantities of Dessaigne's benzotartaric acid.* The oily liquid previously mentioned as being thrown down on acidifying the crude product consists of a mixture of benzoic and ethylbenzoic acids, with a little neutral oil having the odour of benzoic ether.

Therefore by hydrating benzotartaric ether with alcoholic potash, the following reactions take place:—

I. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}C_4H_3(C_7H_5O)O_6 + H_2O = C_2H_6O + \left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}C_4H_3(C_7H_5O)O_6.$

Benzotartaric ether. Alcohol. Ethylbenzotartaric acid.

II. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}C_4H_3(C_7H_5O)O_6 + 2H_2O = 2C_2H_6O + \left.\begin{matrix}H\\H\end{matrix}\right\}C_4H_3(C_7H_5O)O_6.$

Benzotartaric acid.

III. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}C_4H_3(C_7H_5O)O_6 + 3H_2O = 2C_2H_6O + \left.\begin{matrix}H\\H\end{matrix}\right\}C_4H_4O_6 + C_7H_6O_2.$

Tartaric acid. Benzoic acid.

Action of Chloride of Succinyl on Tartaric Ether.

Chloride of succinyl and tartaric ether, when heated together, evolve hydrochloric gas in considerable quantity, and produce a neutral oily body. In preparing this substance, I have generally employed the tartaric ether and chloride of succinyl, in the proportions of two equivalents of the former to one equivalent of the latter. These bodies were heated together in a large test-tube in the water-bath until hydrochloric acid ceased to be evolved. The product, after having been frequently agitated with water for several hours, for the purpose of decomposing any free chloride of succinyl, and removing any tartaric ether that might not have been acted upon, was purified in the same manner as benzotartaric ether. Two combustions in oxygen gave the following numbers:—

I. ·2564 of substance gave
·4487 of CO_2, and
·1343 of H_2O.

II. ·2723 of substance gave
·4772 of CO_2, and
·1426 of H_2O.

* J. Pharm. [3], xxxii, 47.

These numbers give percentages which nearly agree with those required by the formula

$$\begin{matrix}(C_2H_5)_2,C_4\\(C_2H_5)_2,C_4\end{matrix}\left(\begin{matrix}H_3\\C_4H_4O''_2\\H_3\end{matrix}\right)\begin{matrix}O_6\\O_6\end{matrix} = C_{20}H_{30}O_{14}.$$

This represents two equivalents of tartaric ether bound together by the replacement of two equivalents of hydrogen by diatomic succinyl.

The following is a comparison of the theoretical and experimental numbers:—

	Theory.		Experiment. I.	Experiment. II.
C_{20}	240	48·58	47·72	47·79
H_{30}	30	6·07	5·81	5·81
O_{14}	224	45·35	..	..
	494	100·00		

The carbon and hydrogen in these analyses are rather low. This originates, I believe, from the presence of a small quantity of a neutral chlorinated oil, which is generally found in the chloride of succinyl; and on account of the nature of the new product, I was unable to purify it further. A compound representing one equivalent of tartaric ether with two equivalents of hydrogen replaced by succinyl, would require a very much higher percentage of carbon, viz., 53·7.

This product I propose to call *succinotartaric ether*. It is an extremely thick oil, generally of a pale yellow colour, but I believe would be colourless if perfectly pure. It is soluble in alcohol and ether in all proportions, producing solutions which are neutral to litmus paper. If heated with alcoholic potash, it is decomposed. It cannot be distilled without undergoing decomposition.

Action of Chloride of Acetyl on Benzotartaric Ether.

Not succeeding in replacing a second equivalent of hydrogen in tartaric ether, by treating it with chloride of benzoyl, I thought it well to employ a more active chloride, and selected the chloride of acetyl.

A mixture of benzotartaric ether and chloride of acetyl in about equivalent proportions, using a slight excess of the chloride, was heated in a sealed tube to 140° or 150° C. for three or four hours. On opening the tube, large quantities of hydrochloric acid escaped. The oily product was well agitated with water and dissolved in ether. The ethereal solution was then agitated with dry carbonate of sodium, filtered, and evaporated to dryness over the water-bath. A specimen of this product burnt in oxygen gave the following numbers:—

·2332 of substance gave
·4965 of CO_2 and
·1219 of H_2O.

These numbers give percentages which agree very closely with those required by the formula

$$(C_2H_5)_2.C_4H_2(C_7H_5O)(C_2H_3O)O_6 = C_{17}H_{20}O_8,$$

which represents benzo-tartaric ether, in which one equivalent of hydrogen is replaced by acetyl.

	Theory.		Experiment.
C_{17}	204	57·95	58·02
H_{20}	20	5·68	5·80
O_8	128	36·37	..
	352	100·00	

This product which I propose to call *Acetobenzo-tartaric ether*, is an extremely thick colourless oil, heavier than water. It does not show any tendency to solidify, as specimens which have been kept for months remain perfectly clear. It is very soluble in alcohol and ether, and is quite neutral to test-paper. Heated with alcoholic potash, it is entirely decomposed into alcohol, acetic, benzoic, and tartaric acids, thus:

$$\underset{\text{Acetobenzotartaric ether.}}{(C_2H_5)_2C_4H_2(C_7H_5O)(C_2H_3O)O_6} + 4H_2O =$$

$$\underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Tartaric acid.}}{C_4H_6O_6}.$$

Action of Chloride of Acetyl on Tartaric Ether.

Tartaric ether is freely attacked by chloride of acetyl even at

the ordinary temperature, large volumes of hydrochloric acid gas being evolved, and the mixture becoming quite hot. If equivalent proportions of these two substances are employed, an oily body is produced. This product may be purified in the same manner as the aceto-benzo-tartaric ether. Combustion of this oil in oxygen gave the following numbers :—

·2639 of substance gave
·4662 of CO_2 and
·1574 of H_2O,

these numbers give percentages agreeing with the formula

$$(C_2H_5)_2,C_4H_3(C_2H_3O)O_6 = C_{10}H_{16}O_7,$$

which represents tartaric ether with one equivalent of hydrogen replaced by acetyl, as the following comparison will show :—

	Theory.		Experiment.
C_{10}	120	48·38	48·17
H_{16}	16	6·45	6·62
O_7	112	45·17	—
	248	100·00	

This substance, which I propose to call *Aceto-tartaric ether*, is a colourless oil, not nearly so viscid as those already described, being of about the consistency of olive oil. On heating it in a retort placed in an oil-bath, it begins to decompose after the temperature has been considerably raised, acetic acid condensing in the neck of the retort; and at about 287° C. an oil distils over, leaving a residue of carbon.

Aceto-tartaric ether is heavier than water, and slightly soluble in that menstruum. It may be separated from its aqueous solution by the addition of saline solutions, as that of common salt. It is perfectly neutral to test-paper, and has a rather bitter taste.

With boiling aqueous ammonia, aceto-tartaric ether decomposes, and on evaporating the solution, a yellowish syrupy product is obtained, having a bitter and slightly burning taste.

Aceto-tartaric ether, when heated with chloride of benzoyl, evolves hydrochloric acid, forming a thick colourless oil, probably benzoacetotartaric ether.

Sodium acts rapidly upon this ether with evolution of hydro-

gen gas. The reaction is facilitated by the addition of benzole, which renders the ether more fluid. The resulting product of this reaction is a transparent gum-like substance. This is probably *Sodacetotartaric ether.*

On treating tartaric ether with two equivalents of chloride of acetyl, and after the reaction has abated, heating the product in a sealed tube to 100° for a short time, a second derivative is obtained, which, on being purified like the preceding, solidifies after standing, into a beautiful crystalline mass, which may be separated from a small quantity of oily aceto-tartaric ether by pressure between bibulous paper, under a powerful press, and then crystallised from water. Specimens dried by fusion and burnt in oxygen gave the following numbers:—

I. ·2606 of substance gave
·4763 of CO_2 and
·1500 of H_2O.

II. ·2604 of substance gave
·4763 of CO_2 and
·1507 of H_2O.

These numbers give percentages which agree closely with those required by the formula—

$$(C_2H_5)_2,C_4H_2(C_2H_3O)_2O_6 = C_{12}H_{18}O_8,$$

which represents tartaric ether, in which two equivalents of hydrogen are replaced by acetyl.

The following is a comparison of the theoretical and experimental numbers:—

	Theory.		Experiment.	
			I.	II.
C_{12}	144	49·65	49·84	49·88
H_{18}	18	6·20	6·39	6·43
O_8	128	44·15	—	—
	290	100·00		

This substance is therefore *Diacetotartaric ether.* It is soluble in alcohol and ether in all proportions, but crystallises from its alcoholic solution on dilution with water. If boiled with water a considerable quantity dissolves, and the solution, on cooling, deposits it in splendid prismatic crystals, more than an inch and

a half in length. It is slightly soluble in cold water, but on the addition of a strong solution of chloride of sodium, this solution becomes cloudy and the diacetotartaric ether crystallises out on standing.

Diacetotartaric ether melts to a colourless oil at 67° C., and cools without resolidifying, but as soon as a small particle of the solid product is thrown into it, it begins to crystallise in tufts of needles, and in a few moments becomes perfectly solid. During its crystallisation it evolves heat sufficient to become quite hot to the hand.

If strongly heated, this ether distils with only slight decomposition. Its boiling point is between 294° and 298° C. The second combustion was made with a product which had been distilled. I believe this to be the only derivative of tartaric acid which is known to bear distillation without being entirely, or at any rate very much, decomposed.

Diacetotartaric ether is not quickly decomposed with aqueous potash, and if it be dissolved in cold alcoholic ammonia, the solution, after having been kept for several days, will be found to contain a very large quantity of unchanged product.

Fused diacetotartaric ether evolves only a very small quantity of hydrogen when brought in contact with sodium—very much less than the monoacetotartaric ether—in fact its solution in benzole scarcely evolves a trace of hydrogen, and on the evaporation of the benzole, the product is found unchanged. This would tend to show that all the typical hydrogen in tartaric ether is substituted in this compound.

Paratartaric ether yields two new bodies when treated with chloride of acetyl, viz., *acetoparatartaric* and *diacetoparatartaric ether*. They are prepared precisely in the same manner as the two preceding bodies. The monacetoparatartaric ether I have not closely examined. It is a colourless oil. The diacetoparatartaric ether is a solid body, melting at 50·5° C. It boils at about 298° C. and distils with slight decomposition. It is soluble in alcohol or ether in all proportions. It is deposited from its boiling aqueous solution, on cooling, in small tufts of needles, and after long standing sometimes forms short, but very brilliant, prisms on the sides of the vessel.

It differs from the ordinary tartaric derivative in its melting point, which is 16·5 degrees lower, and also in the different

manner in which it crystallises from its aqueous solutions. It appears to be rather more soluble in water, but does not crystallise nearly so freely as its isomer, and when fused it takes much longer to solidify, and then does not produce so well crystallised a mass. A portion of this product gave the following numbers :—

·2063 of substance gave
·3769 of CO_2 and
·1169 of H_2O.

	Percentage composition.	Theory.
Carbon	49·82	49·65
Hydrogen	6·29	6·20

These results show it to possess exactly the same composition as diacetotartaric ether.

I was anxious to take the vapour-densities of these two diaceto-ethers, because, if paratartaric acid be composed of right- and left-handed tartaric acids, its formula should be doubled, and this difference a vapour-density would show directly; but although these bodies are volatile they would decompose too much at the temperature required by such experiments, to give trustworthy results; but the boiling points being nearly identical, affords strong evidence that the formula must not be altered, because if it were double, it is certain that the boiling point would be immensely raised. I may here mention that diacetoparatartaric ether, after having been distilled, has exactly its original characters and fusing point.

It is very curious to find that paratartaric acid, which yields right- and left-handed tartaric acids, and is also formed again when their solutions are mixed even with evolution of heat, does not possess a formula equal to two equivalents of tartaric acid. It would appear therefore not to consist of these two acids, but to change into them when converted into certain salts.

Action of Chloride of Acetyl on Tartaric Acid.

If dry, powdered tartaric acid be digested with about three times its weight of chloride of acetyl, very little change appears to take place at first, but after continuing the heat for several hours it gradually disappears, leaving a syrupy liquid,

which on cooling generally solidifies to a crystalline mass; should this not take place, more chloride of acetyl must be added. The crystalline product, after being strongly pressed between dry, thick bibulous paper, may be rendered perfectly pure by fusion in an open dish, so as to volatilize adhering chloride of acetyl, &c.

On cooling, it solidifies to a splendid white crystalline body.

Specimens of this substance burnt in oxygen gave the following numbers:—

I. ·2539 of substance, gave
·4122 of CO_2, and
·0907 of H_2O.

II. ·2438 of substance, gave
·3974 of CO_2, and
·0862 of H_2O.

These numbers give percentages which agree with those required by the formula—

$$C_4H_2(C_2H_3O)_2O_5 = C_8H_8O_7,$$

representing *diacetotartaric anhydride.*

The following is a comparison of the numbers:—

	Theory.		Experiment.	
			I.	II.
C_8	96	44·44	44·27	44·45
H_8	8	3·70	3·96	3·93
O_7	112	51·86	—	—
	216	100·00		

Diacetotartaric anhydride is a tough crystalline solid, melting at 126°—127° C. When distilled it undergoes a considerable amount of decomposition, especially if the distillation be carried on slowly. It boils above 250° C., but no fixed point can be obtained, acetic anhydride coming over during the distillation, as well as other products, some of which affect the eyes like acrolene; a residue of carbon is left in the retort. If heated gently, it sublimes in beautiful, but small prisms. It is slightly soluble in benzole, and crystallises from this solvent in slender white needles. It also crystallises from acetic anhydride.

Dried paratartaric acid, when submitted to the action of

chloride of acetyl, undergoes precisely the same change as ordinary tartaric acid, but the reaction goes on rather more slowly. The *diacetoparatartaric anhydride* is a beautiful crystalline body, resembling its isomer in its characters. Its melting-point is also the same, viz., 126° C.

The following is a combustion of a specimen of diacetotartaric anhydride prepared from paratartaric acid :—

·3012 of substance, gave
·4873 of CO_2, and
·1056 of H_2O.

Percentage composition—

		Theory.
Carbon.....	44·12	44·44
Hydrogen	3·89	3·70

Action of Water on Diacetotartaric Anhydride.

If exposed to the air, this anhydride quickly absorbs moisture, or if placed in contact with warm water, it gradually dissolves, producing a powerfully acid solution. This contains an acid which I propose to call *diacetotartaric acid*. Its formation may be explained thus :—

$$\underset{\text{Diacetotartaric anhydride.}}{C_4H_2(C_2H_3O)_2O_5} + H_2O = \underset{\text{Diacetotartaric acid.}}{C_4H_4(C_2H_3O)_2O_6}.$$

Diacetotartaric acid, obtained by evaporating its aqueous solution under the bell-jar of an air-pump, generally presents itself as a transparent gum-like substance. It is very deliquescent, and possesses a powerfully acid taste. If strongly heated, it decomposes without formation of its anhydride.

When heated with a solution of potash or soda, it is decomposed according to the following equation :—

$$\underset{\text{Diacetotartaric acid.}}{C_4H_4(C_2H_3O)_2O_6} + 2H_2O = \underset{\text{Tartaric acid.}}{C_4H_6O_6} + \underset{\text{Acetic acid.}}{2C_2H_4O_2}.$$

A quantity of diacetotartaric acid which had been prepared from *ordinary tartaric acid*, was decomposed by potash, and after neutralising with an acid, the tartaric acid was precipitated as a calcium-salt, which, after being well washed, was decomposed with dilute sulphuric acid and filtered. The filtrate on being con-

centrated, deposited large crystals of tartaric acid which were washed and recrystallised.

The acid thus obtained does not contain water of crystallisation, nor does it precipitate solutions of chloride or nitrate of calcium; it would therefore appear to be ordinary tartaric acid, but it appears to crystallise in a somewhat different manner. As I have obtained it in square tables, about a quarter of an inch in diameter, I hope to again examine this product.

A portion of the acid was converted into the acid potassium-salt. A potassium determination gave the following numbers:—

·1219 of substance, gave
·0557 of sulphate of potassium

= 20·47 p. c. of potassium. Theory requires 20·74 p. c.

Diacetotartrates.—With bases, diacetotartaric acid forms salts containing one and two equivalents of metal,—it is therefore bibasic. These compounds are rather difficult to obtain pure, and are remarkable for their great solubility.

Sodium-salt.—This is obtained by carefully neutralising a solution of the acid with carbonate of sodium, concentrating at a very gentle heat, and then finally evaporating in vacuo. Thus obtained, it is a crystalline solid, remarkably soluble in water, and very deliquescent.

The potassium-salt is obtained in the same manner as the above, substituting carbonate of potassium for carbonate of sodium. It is a crystalline salt, very soluble in water, and deliquescent.

Acid potassium-salt $\left.\begin{matrix}K\\H\end{matrix}\right\}C_8H_8O_8$.—To prepare this salt two equal quantities of an aqueous solution of the acid are taken, one portion is neutralised with carbonate of potassium, and then mixed with the other. The new salt crystallises out on concentrating the solution at a gentle heat, or in vacuo; it is then separated from the mother-liquor by being strongly pressed between bibulous paper and purified by a second crystallisation. Thus obtained, it forms a crystalline powder, very soluble in water, but not deliquescent. It reddens litmus powerfully, and possesses an acid taste. A specimen dried at 100° C. gave the following numbers:—

0·3415 of substance, gave
0·1080 of sulphate of potash,

= 14·17 p. c. of potassium. Theory requires 14·34 p. c.

Calcium-salt, $Ca''C_8H_8O_8$.—This salt is obtained by neutralising a solution of the acid with carbonate of calcium, filtering and concentrating first at a low heat and then in vacuo. I have not succeeded in obtaining it in a crystalline condition. Its solution concentrates to a syrup, and then dries up to an opaque friable mass. It is deliquescent.

A specimen dried at 100° C. gave the following numbers :—

·1871 of substance, gave
·0951 of sulphate of calcium,

= 14·94 p. c. of calcium. Theory requires 14·70 p. c. of calcium.

Barium-salt, $Ba''C_8H_8O_8$.—This is obtained in the same manner as the calcium-salt. Its solution, after being concentrated to a syrup, on standing for a day or two, deposits fine needles of this new salt, sometimes half an inch in length. It is excessively soluble in water, and deliquescent. Specimens dried at 100° C. gave the following numbers :—

I. ·2065 of substance, gave
·1297 of sulphate of barium.

II. ·1377 of substance, gave
·1307 of CO_2, and
·0300 of H_2O.

The following is a comparison of the theoretical and experimental numbers :—

	Theory.		Experiment. I.	Experiment. II.
C_8	96	26·01	—	25·88
H_8	8	2·17	—	2·34
Ba''.....	137	37·12	36·93	—
O_8	128	34·70	—	—
	369	100·00		

Copper-salt, $Cu''C_8H_8O_8$.—Obtained by saturating a solution of the acid with carbonate of copper, and concentrating the solution at a low temperature. It is a blue crystalline salt, very soluble in water. Specimens dried at 100° C. gave the following numbers :—

I. ·3527 of substance gave
·0945 of $Cu''O$ = 21·40 p. c. of copper.

II. ·2268 of substance gave
·0603 of CuO = 21·22 p. c. of copper.
Theory requires 21·48 p. c. of copper.

Silver-salt, $Ag_2C_8H_8O_8$.—Diacetotartaric acid is difficult to saturate with carbonate of silver. To obtain this salt, it is best to agitate a solution of the acid with freshly precipitated carbonate of silver, filter, and concentrate. After a time the silver-salt will then separate in the form of an albuminous magma of very minute silky needles, which must be separated from the mother-liquor by pressure between bibulous paper, and then recrystallised. Thus obtained, it dries to a white crystalline mass, extremely soluble in water, and very slowly acted upon by light.

Mercury-salt.—A solution of mercurous nitrate when added to a solution of a salt of diacetotartaric acid, produces a gelatinous precipitate soluble in acetic acid.*

Diacetoparatartaric anhydride, when brought in contact with water, yields an acid, viz., *diacetoparatartaric acid*. So far as I have examined this body, it appears to resemble diacetotartaric acid, but when decomposed with potash, it yields acetic and *paratartaric acids*. This at once proves that it and its anhydride are isomers of the ordinary tartaric derivatives, a fact which it was important to prove, on account of diacetotartaric and diacetoparatartaric anhydrides having the same melting point.

A portion of diacetoparatartaric acid was converted into a calcium-salt, which was dried at 100°; a calcium determination gave the following numbers:—

·2240 of substance gave
·1092 of sulphate of calcium = 14·33 per cent.
Theory requiring 14·7 per cent.

This salt was uncrystallisable.

Action of Sodium on Tartaric Ether.

On bringing sodium in contact with tartaric ether, hydrogen

* Since making the foregoing experiments, I find that M. Rochleder has also studied the behaviour of chloride of acetyl to tartaric acid, and evidently obtained some of the bodies described above. He did not, however, make any analysis of his products. He states that he succeeded in obtaining the acid I have described as diacetotartaric acid in the crystalline state (Chemical Gazette, vol. xvii. (1859), page 51).

is evolved; but owing to the viscidity of the ether, the reaction takes place very slowly. If, however, it be rendered more fluid by admixture with five or six times its volume of anhydrous benzole, the reaction goes on very rapidly, the liquid becoming quite hot and of a pale yellow colour. On separating the excess of sodium and evaporating the liquid, a pale yellowish-brown uncrystalline, but friable residue is obtained, which quickly becomes sticky from absorption of moisture; mixed with water, it produces a strongly alkaline solution.

A weighed quantity of tartaric ether was treated as above in an apparatus so arranged that the hydrogen could be collected. It was found that the reaction went on rapidly for about half an hour, until nearly one equivalent of hydrogen was evolved; it then slackened, the solution remaining clear, and the sodium quite bright. The action then became still less, and a gelatinous product gradually formed on the sodium entirely stopping the reaction.

Reasoning from these facts, it would appear that the first and principal product of this reaction is a tartaric ether, with one equivalent of hydrogen replaced by sodium, or *sodiotartaric ether*, the gelatinous product being *disodiotartaric ether*.

By heating the first sodium-product with iodide of ethyl, an oil is produced, probably *ethyltartaric ether*.

The history of the foregoing substances has, I think, a considerable amount of theoretical interest, especially with reference to that somewhat difficult question of basicity and atomicity.

Tartaric acid is known to be tetratomic; now if it be likewise tetrabasic, it is evident that tartaric ether must be a bibasic acid, diethyltartaric acid, because only two equivalents of hydrogen out of four are replaced by ethyl, thus—

$H_4,C_4H_2O_6$.	$H_2,E_2,C_4H_2O_6$.
Tartaric acid.	Diethyltartaric acid.

If this be true, then most of the products I have described would be diethyltartrates. For example, the substance I have called diacetotartaric ether would be diethyltartrate of acetyl; thus—

$H_2,E_2,C_4H_2O_6$.	$Ac_2,E_2,C_4H_2O_6$.
Diethyltartaric acid.	Diethyltartrate of acetyl.

If this be the case, it is obvious that this body would be an

anhydride, because anhydrides containing monatomic acid radicals are but the salts of acid radicals; acetobenzoic anhydride, for example, is the acetate of benzoyl. But this substance has not in any respect the characteristics of this class of bodies. Were it an anhydride or salt of acetyl, it would easily decompose with water, and still more so if treated with ammonia; whereas it may be boiled in water and recrystallised without undergoing any change, and its alcoholic solution may also be saturated with ammonia, and left for days without any appreciable amount of decomposition taking place.

The same facts also hold true with benzotartaric ether; and, moreover, when we decompose this product with a limited quantity of alcoholic potash, we find that the ethyl is removed much more readily than the benzoyl, ethylbenzotartaric acid and then benzotartaric acid being formed. Had it been a diethyltartrate of benzoyl, it would immediately have split up into tartaric ether and benzoate of potassium.

Benzotartaric ether also, if heated with ammonia, does not produce benzamide.

The properties of diacetotartaric anhydride are also against this view. This anhydride rapidly absorbs water, forming diacetotartaric acid, and this acid, containing two equivalents of acetyl, a radical so very easily hydrated when replacing basic hydrogen, may be heated up to 100° C. with water without undergoing any appreciable amount of decomposition; moreover, it forms salts which may be dried at 100° C. without change.

The properties of tartaric ether itself are also against this view, as it is perfectly neutral to test-paper, and does not form compounds with bases.

We have therefore, I think, strong evidence that, although tartaric acid is tetratomic, yet the two pair of hydrogen equivalents possess very different functions.

The nature of this difference may, I think, be well understood by examining into the particulars of the artificial formation of this acid from succinic acid.

Maxwell Simpson* has lately shown that succinic acid is a derivative of ethylene, and may be produced by heating the cyanide of that hydrocarbon with potash.†

* Chem. Soc. J., xv, 134.

† The formation of malonic acid from cyanacetic acid is analogous to this

$$\left(\begin{matrix}C_2N_2\\C_2H_4''\end{matrix}\right) + 4H_2O = \left(\begin{matrix}(COHO)_2\\C_2H_4''\end{matrix}\right) + 2NH_3.$$

Cyanide of ethylene. Succinic acid.

On treating succinic acid with bromine, two equivalents of hydrogen are replaced. This replacement must evidently take place in the ethylene, because the resulting acid retains its two original basic hydrogens;

$$\left(\begin{matrix}(COHO)_2\\C_2H_4''\end{matrix}\right) + 2BrBr = \left(\begin{matrix}(COHO)_2\\C_2H_2\\Br_2\end{matrix}\right\}'' + 2HBr.$$

Succinic acid. Bibromosuccinic acid.

By boiling the bibromosuccinate of silver with water, the two equivalents of bromine are removed and HO substituted.

$$\left(\begin{matrix}(COHO)_2\\C_2H_2\\Br_2\end{matrix}\right\}'' + 2H_2O = \left(\begin{matrix}(COHO)_2\\C_2H_2\\H_2\end{matrix}\right\}''O_2.$$

Bibromosuccinic acid. Tartaric acid.

From this it will be seen that tartaric acid is succinic acid, in which ethylene C_2H_4'' is replaced by $\left.\begin{matrix}C_2H_2\\H_2\end{matrix}\right\}''O_2$, which represents the hydrate of acetylene, or acetylene-glycol, which in this case has all its atomicity active, and holds together the two groups of (COHO). This shows tartaric acid to be a bibasic acid and diatomic alcohol.

Therefore the hydrogen which I have replaced in tartaric ether by acid radicals, is not basic hydrogen, but alcoholic hydrogen. Each of the tartaric ether derivatives will then have the *double* character of an ether and the hydrin of a glycol, and those from tartaric acid the double character of an anhydride or

reaction, as will be seen if we start with the cyanide of methylene, and stop the reaction at an intermediate stage.

$$CH_2CyCy + 2H_2O = C_2(H_3Cy)O_4 + NH_3.$$

Cyanacetic acid.

$$C_2(H_3Cy)O_4 + 2H_2O = C_3H_4O_4 + NH_3.$$

Chem. Soc. J. [2], ii, 109.

an acid and hydrin of a glycol. This will be best seen if I write out their formulæ in the following manner*:—

Tartaric ether ..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ H_2\end{matrix}\right\}'' O_2.\right)$

Benzotartaric ether ..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ H \\ Bz\end{matrix}\right\}'' O_2.\right)$

Ethylbenzotartaric acid .. $\left(\begin{matrix}COHO \\ COEO \\ C_2H_2 \\ H \\ Bz\end{matrix}\right\}'' O_2.\right)$

* It is worth remarking that tartaric bears to succinic acid a relation similar to that of glycollic acid to acetic acid. It is, in fact, a bibasic glycollic acid.

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} - O_2 = \underset{\text{Succinic acid.}}{C_4H_6O_4}.$$

$$\underset{\text{Glycollic acid.}}{C_2H_4O_3} - O = \underset{\text{Acetic acid.}}{C_2H_4O_2}.$$

And as glycollic acid represents glycol half oxidized, so tartaric acid represents a tetratomic alcohol half oxidized.

$$\underset{\text{Glycol.}}{C_2H_6O_2} + O_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3} + H_2O.$$

$$C_4H_{10}O_4 + O_4 = \underset{\text{Tartaric acid.}}{C_4H_6O_6} + 2H_2O.$$

This alcohol would be the same body as that termed tartaric alcohol in Kolbe's paper on the prognosis of new alcohols and aldehydes (Chem. Soc. J. [2], iv, 56).

It will be observed that tartaric acid has the composition of oxalic acid + acetylene-glycol, thus:—

$$\left(\begin{matrix}COHO \\ COHO \\ C_2H_2 \\ H_2\end{matrix}\right\}O_2\right) = \underset{\text{Oxalic acid.}}{\begin{matrix}H_2 \\ C_2O_2''\end{matrix}\Big\}O_2} + \underset{\text{Acetylene glycol.}}{\begin{matrix}H_2 \\ C_2H_2''\end{matrix}\Big\}O_2}.$$

Tartaric acid.

I have already made several experiments with the view of causing the two groups of COHO to combine and liberate the glycol, but as yet have not succeeded.

Acetobenzotartaric ether .. $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ Ac \\ Bz\end{matrix}\right\}''O_2\cdot\Bigg)$

Acetotartaric ether ..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ H \\ Ac\end{matrix}\right\}''O_2\cdot\Bigg)$

Diacetotartaric ether..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ Ac \\ Ac\end{matrix}\right\}''O_2\cdot\Bigg)$

Succinotartaric ether..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ H \\ Su'' \\ H \\ C_2H_2 \\ (COEO)_2\end{matrix}\right\}''O_2\cdot\Bigg)$

Diacetotartaric anhydride.. $\left(\begin{matrix}CO'' \\ CO'' \\ C_2H_2 \\ Ac \\ Ac\end{matrix}\right\}O\Bigg)$

Diacetotartaric acid ..... $\left(\begin{matrix}(COHO)_2 \\ C_2H_2 \\ Ac \\ Ac\end{matrix}\right\}''O_2\cdot\Bigg)$

Sodiotartaric ether ..... $\left(\begin{matrix}(COEO)_2 \\ C_2H_2 \\ H \\ Na\end{matrix}\right\}''O_2\cdot\Bigg)$?

According to the foregoing reasoning, the metallic compounds representing tartaric acid as tetrabasic (if definite bodies), must be both salts and alcoholates. The lead-salt might be thus written:—

$$\left(\begin{matrix}(COPbO)_2 \\ C_2H_2 \\ Pb_2\end{matrix}\right\}''O_2\Bigg).$$

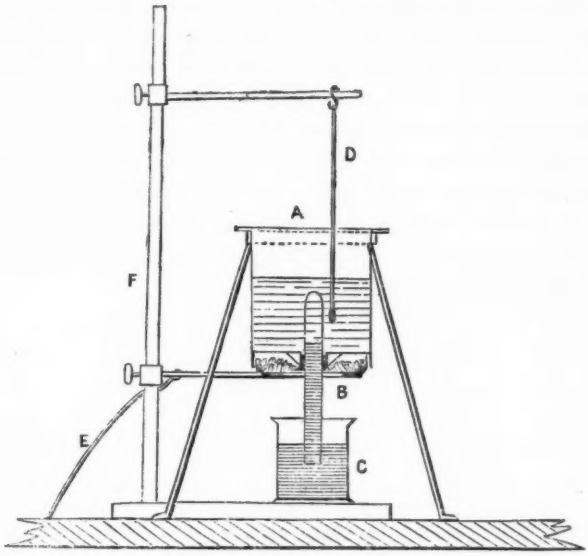
Seeing then the great difference in the properties between the compounds in which basic hydrogen is replaced by acid radicals, from those in which alcoholic hydrogen is replaced, it appears to me that this points out a very useful method of determining the true basicity of an acid as well as its alcoholic nature, if it possesses any,—and this is important, because the alcohols of some series, *i. e.*, the aromatic series, are capable of combining with bases; therefore an acid of such a series, if possessing alcoholic characters, would produce saline compounds, making its basicity appear greater than it actually is, thereby preventing us from classifying it with analogous bodies of other series. I believe this to be the case with salicylic acid, and I am now engaged with experiments in this direction, which I hope shortly to lay before the Society.

XI.—*On the Absorption of Vapours by Charcoal.*

By JOHN HUNTER, M.A., F.C.S., Chemical Assistant, Queen's College, Belfast.

THE paper which I had the honour of laying before the Chemical Society, early last session, contained the results of a series of experiments on the absorption of vapours by cocoa-nut charcoal. Since that time I have determined a large number of absorptions, which are given in the present paper. In consequence of the difficulty of using a liquid having a much higher boiling point than oil of turpentine in the apparatus previously described, it was necessary to adopt an altogether different method, which would enable me to observe the absorption of vapours heated in a bath of paraffin. For this purpose a copper vessel A was employed into which the absorption tube B was introduced by means of a tightly-fitting cork. The neck into which the cork was fixed, consisted of a cone-shaped double chamber, which allowed the melted paraffin to flow in between the two surfaces, so as to protect the cork from being destroyed by the heat of the gas. The sides of the vessel extended below the bottom in order to prevent the flame flaring up on the outer surface. The heat was applied to the bath by

means of a hollow ring supplied with gas-jets, which fitted on the stand F. The lower extremity of the absorption-tube dipped into a carefully graduated glass vessel C filled with mercury.



In performing an experiment, the graduated absorption-tube B was first introduced into the paraffin bath A, and securely fastened by means of the cork; it was then filled with mercury and inverted in the glass vessel C. The level of the mercury in C was observed, the capsule containing the liquid whose vapour-absorption was to be examined introduced into the tube B, and heat applied to the copper vessel. When the desired temperature was indicated by the thermometer D suspended in the paraffin bath, the mercurial level in C was again read, and the charcoal introduced as in the former experiments. As the absorption proceeded, the mercury was depressed in C, and when this remained constant the level was again observed. The value of the divisions of the absorption-tube B being known, the difference in height of the mercury in the tube and bath could be determined, and the absorption deduced by a simple calculation.

In the following tables containing the vapour-absorptions at various temperatures, it will be noticed that from 195° C. to

200° C., one volume of cocoa-nut charcoal absorbs 110·7 volumes of vapour of aniline, 102·0 of carbolic acid, and 101·1 of hydride of benzoyl.

I have examined the absorption of several vapours by means of the apparatus described in a former paper and found that aldehyde, acetic ether and acetone, are absorbed respectively, 138·7, 116·0, and 104·6 at 100° C. by one volume of cocoa-nut charcoal.

In the tables, V represents the number of volumes of the vapour absorbed by one volume of cocoa-nut charcoal at the temperature and pressure at which the experiment is performed. T and $\acute{T}$ are the initial and final temperatures; P and $\acute{P}$ the pressures deduced by subtracting the difference in level from the height of the barometer.

ANILINE.

	V	T	$\acute{T}$	P	$\acute{P}$
	113·6	196·5	201·3	604·3	587·0
	108·0	200·0	202·5	602·3	600·8
	110·5	194·0	193·0	603·2	588·2
Mean....	110·7	196·8	199·1	603·3	592·0

CARBOLIC ACID.

	106·2	197·3	197·5	596·8	592·3
	100·0	195·0	191·0	604·3	585·4
	100·0	193·5	193·5	590·1	577·4
Mean....	102·0	195·3	194·0	597·1	585·0

HYDRIDE OF BENZOYL.

	101·8	195·7	198·0	551·8	542·9
	100·0	192·5	191·0	577·8	568·5
	101·6	202·0	200·5	582·8	573·3
Mean....	101·1	196·7	196·5	570·8	561·5

BUTYRIC ACID.

	83·0	195·3	194·5	591·1	575·4
	83·3	197·0	199·2	592·8	577·6
	88·8	199·2	199·3	575·1	556·9
	82·1	197·7	197·0	585·6	570·1
Mean....	84·3	197·3	197·5	588·1	570·0

BUTYRIC ETHER.

	72·0	201·0	199·0	596·3	591·4
	77·7	192·0	191·5	599·6	590·8
	75·0	198·7	197·0	605·9	600·0
Mean....	74·9	197·2	195·8	600·6	594·1

OIL OF TURPENTINE.

	V		T	$\dot{T}$		P	$\dot{P}$
	50·1	....	197°·7	192°·3	....	584·0	576·3
	45·5	....	195·4	195·0	....	597·5	593·8
	48·4	....	192·7	192·7	....	582·5	573·5
Mean....	48·0	....	195·8	193·0	....	588·3	581·2

VALERIANIC ACID.

	40·9	....	198·0	198·0	....	575·5	569·5
	41·3	....	198·0	197·0	....	591·3	581·1
	41·4	....	197·5	197·0	....	577·8	573·1
Mean....	41·2	....	197·8	197·3	....	581·5	574·5

ALDEHYDE.

	61·6	....	155·0	157·2	....	693·0	695·0
	67·7	....	153·5	155·5	....	673·0	675·1
	67·9	....	154·7	156·5	....	689·3	699·3
	69·4	....	154·0	151·0	....	679·3	677·8
Mean....	66·6	....	154·3	155·0	....	683·9	686·8
	136·9	....	100·0	100·0	....	688·0	673·5
	137·5	....	100·0	100·0	....	689·5	682·5
	141·7	....	100·0	100·0	....	684·0	686·5
Mean....	138·7	....	100·0	100·0	....	687·1	680·8

ACETIC ETHER.

	72·7	....	154·0	155·0	....	697·5	688·5
	72·4	....	155·5	154·5	....	691·0	672·5
	69·4	....	153·0	151·2	....	686·5	675·0
Mean....	71·5	....	154·1	153·6	....	691·7	678·7
	118·0	....	100·0	100·0	....	695·2	677·2
	112·8	....	100·0	100·0	....	675·5	663·2
	114·5	....	100·0	100·0	....	660·5	662·5
	119·0	....	100·0	100·0	....	674·3	658·0
Mean....	116·0	....	100·0	100·0	....	676·4	665·2

ACETONE.

	63·5	....	156·5	156·0	....	694·7	674·7
	59·9	....	155·5	157·0	....	688·8	674·3
	73·7	....	157·0	158·0	....	692·0	666·5
	75·2	....	155·0	156·3	....	688·8	669·3
Mean....	68·0	....	156·0	156·8	....	691·1	671·4
	100·8	....	100·0	100·0	....	665·5	649·4
	102·6	....	100·0	100·0	....	655·7	648·7
	108·0	....	100·0	100·0	....	644·5	643·5
	101·3	....	100·0	100·0	....	650·5	627·0
	105·0	....	100·0	100·0	....	644·8	631·3
	109·0	....	100·0	100·0	....	661·7	650·2
	105·3	....	100·0	100·0	....	660·0	644·0
Mean....	104·5	....	100·0	100·0	....	654·6	641·9

NITROUS ETHER.

	V		T	$\acute{T}$		P	$\acute{P}$
	60·1	....	100·0	100·0	....	666·2	661·2
	64·7	....	100·0	100·0	....	661·2	671·7
	68·7	....	100·0	100·0	....	655·0	655·0
	62·4	....	100·0	100·0	....	656·5	656·5
	62·2	....	100·0	100·0	....	665·5	658·5
Mean....	63·5	....	100·0	100·0	....	660·8	660·6

HYDROCHLORIC ETHER.

	63·0	....	100·0	100·0	....	673·1	678·6
	56·8	....	100·0	100·0	....	668·6	655·6
	60·5	....	100·0	100·0	....	674·3	671·8
	56·9	....	100·0	100·0	....	671·5	662·5
	64·7	....	100·0	100·0	....	675·3	673·8
Mean....	60·4	....	100·0	100·0	....	672·5	668·4

FORMIC ACID.

	30·4	....	158·0	160·0	....	707·8	697·8
	31·5	....	155·3	157·5	....	695·0	688·5
	30·7	....	156·0	157·5	....	687·5	681·0
Mean....	30·7	....	156·4	158·3	....	696·7	689·1

AMYLENE.

	16·5	....	155·0	156·0	....	662·5	656·0
	22·6	....	155·0	154·7	....	640·3	643·3
	16·2	....	156·0	156·0	....	655·0	658·0
Mean....	18·4	....	155·3	155·5	....	652·6	652·4

PERCHLORIDE OF CARBON.

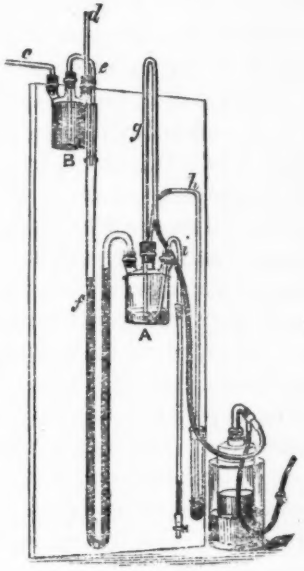
	3·2	....	154·0	154·0	....	706·0	702·5
	4·1	....	154·5	154·5	....	692·2	685·7
	3·8	....	155·0	155·0	....	696·8	695·3
Mean....	3·7	....	154·5	154·5	....	698·3	694·5
	8·2	....	100·0	100·0	....	681·2	687·7
	7·8	....	100·0	100 0	....	678·7	679·2
	7·9	....	100·0	100·0	....	687·5	690·5
Mean....	7·9	....	100·0	100·0	....	682·4	635·8

XII.—*On a New Form of Aspirator.*

By HERBERT M^cLEOD.

THE apparatus consists of two principal parts, A the aspirator proper and B the reservoir, from which the aspirator is replenished with water. The Woulfe's bottle B is connected by

the tube *c* to the water supply, the pressure on which should be as constant as possible; to the other necks of this bottle are fitted a small tube, *d*, open at both ends and just passing through the cork, and a rather wide syphon, *e*, the shorter limb of which reaches nearly to the bottom of the bottle, the longer limb being placed in a wide tube, *f*, extending downwards, to a distance that will presently be indicated, returning upwards and terminating in one of the necks of the Woulfe's bottle, A. The middle neck of bottle A is fitted with a cork carrying two tubes, one, *g*, reaching to the bottom of the bottle, and the other, *h*, passing just through the cork, and being bent twice at right angles at about two decimeters above the neck of the bottle, and dipping into a small quantity of water in a test tube. The third neck of bottle A is provided with a syphon, *i*, having a long limb, from which the water is discharged. The length of the long limb of this syphon must be determined by the amount of suction required. The distance between the bend of the tube, *f*, and the neck of the bottle A, the length of *g* above the cork and the distance between the bend of *h*, and the surface of the water in the test tube should all be about two decimeters greater than the length of the long limb of the syphon, *i*.



To use the apparatus, water is admitted into the bottle B through *c*; as soon as the bottle is filled, the syphon, *e*, is started, which empties the bottle; the water flowing through *f* into A, the air which this vessel contained being expelled through *h* and passing through the water-valve in the test-tube. When A is filled, the syphon, *i*, is set in action, and the water contained in A is replaced by air aspirated through *g*. In the mean time, the reservoir, B, is being filled.

It will be seen from this description that the aspiration is intermittent. The time of inaction may be diminished by regu-

lating the flow from the syphon, *i* (by a compression cock), in such a manner that A is emptied just before B is filled. But the aspiration may be made perfectly constant by connecting the tube *g* with a bell-jar standing in water, and regulating the aspiration by a stop-cock placed between the bell jar and the apparatus through which the air is being drawn: in this case the water will be raised in the bell-jar during the exit of water from A, and will sink, and so continue the aspiration, whilst the bottle A is being refilled.

The quantity of gas aspirated in any length of time may be readily determined by first ascertaining the amount aspirated during each exhaustion, and then by observing the time between each overflow of the syphon, *e*. This interval will be found very constant, and the number of exhaustions which have taken place between any two given times may readily be calculated, and from these data the amount of air aspirated.

The apparatus may be employed either for slow or for rapid aspirations. The one already constructed aspirates half a litre at each exhaustion; with a narrow syphon at *e*, it may be worked as slowly as once in 30 minutes, and, with a wide syphon, as quickly as once in 30 seconds. With a larger apparatus a more rapid aspiration could no doubt be obtained.

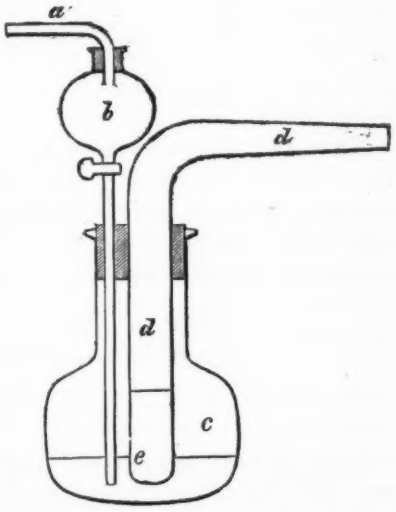
This aspirator has the disadvantage of employing a larger volume of water than it aspirates of air, and its arrangement is rather complex; but, on the other hand, it is composed of materials which every chemist has at hand and it furnishes means of measuring the quantities of gas aspirated.

XIII.—*On some Reactions of Hydriodic Acid.*

By Ernest Theophron Chapman.

In a paper published in the Journal of this Society, August, 1866, "On some Decompositions of Nitrite of Amyl," I stated that the nitrite is decomposed by hydriodic acid, iodide of amyl and nitric oxide being formed; but I have since determined exactly the amount of nitric oxide liberated in this reaction, and find that it falls far short of that required on the assump-

tion that all the nitrogen is liberated in this form. $C_5H_{11}NO_2$ contains 11·966 per cent. of nitrogen, and should therefore yield 25·64 per cent. of NO. I have, as will be seen below, only been able to obtain about 18 per cent. These quantitative experiments were performed in the apparatus figured below. *b* is a stop-cock bulb-tube connected with an apparatus generating hydrogen. Its tube passes through the cork and nearly to the bottom of the flask, *c*, which contains strong hydriodic acid. *d d* is a wide tube sealed at the bottom and having a small hole at *e*. *d* is in connection with a potash apparatus containing caustic potash. This is connected with a chloride-of-calcium tube, and this again, with another potash-apparatus containing protochloride of iron. Finally, this second potash-apparatus is in connection with a small tube containing caustic potash in small lumps. To use the apparatus, it is first completely filled with hydrogen, and the strong hydriodic acid in *c* gently warmed. The stop-cock is then turned off, the tube *a* is removed from the bulb, and the bulb filled with carbonic acid. A weighed quantity of the nitrite is then introduced into the bulb, and the hydrogen-tube at once replaced. The apparatus now contains no air, so that the nitric oxide cannot be oxidized after it is once formed. The stop-cock is then turned on, and the nitrite of amyl allowed to run into the tube. It does not immediately run into the hydriodic acid, but, if the stop-cock be immediately closed, remains suspended in the tube. It is allowed to pass very slowly into the hydriodic acid, by cautiously opening the stop-cock. Nitric oxide is at once evolved and escapes through the small aperture *e*, which is now exactly on a level with the surface of the hydriodic acid, the hydrogen with which the apparatus was filled having forced the hydriodic acid, which was originally above the aperture, into the wide



tube, *d*. The gas escapes in a series of very small bubbles and is of course thoroughly washed by its ascent through the column of liquid in the tube. It passes through the potash and finally into the solution of protochloride of iron, where any nitric oxide is of course immediately absorbed. When all the nitrite has been forced into the hydriodic acid, the bulb *b* is heated, and hydrogen gas again transmitted through the liquid. In this way the last traces of nitrite are forced to pass into the hydriodic acid. The hydriodic acid itself is then heated almost to boiling, and the first set of potash-bulbs are surrounded by hot water, the stream of hydrogen being still continued for a few minutes. The chloride-of-iron bulbs with their accompanying potash tube are then detached and weighed. As they have been weighed previously, the difference in weight shows at once the amount of nitric oxide absorbed.

In one experiment (A) ·8036 of nitrite gave ·1476 of NO. Therefore 18·37 per cent. of NO. The hydriodic acid remaining in the flask was treated with excess of caustic potash and distilled into a standard solution of sulphuric acid, as it was probable that ammonia had been formed. This was found to be the case, and, from the amount of sulphuric acid neutralized, it appeared that 0·0326 of NH_3 had been produced. If we calculate from these data the total amount of nitrogen present we obtain the following results :—

From the nitric oxide	0·06888
From the ammonia	0·02684
Total nitrogen found	0·09572

Therefore the total percentage of nitrogen found is 11·91. In a second experiment (B) conducted in precisely the same manner, ·9646 of nitrite furnished ·1708 of NO and ·0415 of NH_3. We had therefore 17·706 per cent. of NO. Calculating from these results, we find,—

From the nitric oxide	0·07971
From the ammonia	0·03418
	0·11389

Therefore the total percentage of nitrogen found was 11·81. The theoretical percentage of nitrite is 11·966.

That this method of estimating nitric oxide is trustworthy, I have proved by actually liberating a known quantity of nitric oxide from its solution in perchloride of iron, and estimating it in the manner described in the foregoing section. Though somewhat foreign to the subject, the details of the following experiment prove beyond all question the soundness of this statement. I mentioned in the paper already quoted, that nitrite of amyl is decomposed by sulphuric acid, valerianate of amyl, water, nitric oxide, and sulphurous acid being produced. Thus :—

$$2C_5H_{11}NO_2 + H_2SO_4 = 2H_2O + SO_2 + 2NO + C_5H_9(C_5H_{11})O_2.$$

I have determined the amount of protoxide liberated under these circumstances. The apparatus employed was in every respect similar to that already described, sulphuric acid being substituted for hydriodic acid. At the close of the experiment, water was added to the contents of the flask by means of the bulb-tube, thereby diluting the sulphuric acid, and liberating the nitric oxide which the concentrated acid would otherwise have retained. In order to prevent an undue rise of the acid in the wide tube *d*, the flask was tilted during and after the addition of the water. In this manner, ·7962 of nitrite caused an increase of the weight of the second set of potash-bulbs of ·1998. This corresponds to 25·09 per cent. of NO, or 11·71 of N, the theoretical numbers being respectively 25·64, and 11·966.

With these data before me, it appeared worth while to attempt the conversion of nitric oxide into ammonia. With this object, the nitric oxide was transmitted through boiling concentrated hydriodic acid. It was slowly absorbed, and iodine was liberated. To prevent this, a little phosphorus was added. The contents of the vessel were then poured off from the phosphorus, and excess of potash added. The smell of ammonia was immediately perceptible. It was distilled into dilute sulphuric acid, and the distillate evaporated down to a small bulk, and strong alcohol added. This at once occasioned a precipitate of sulphate of ammonium.

It appeared to me to be of interest, also, to determine the action of hydriodic acid on the *nitrates* of the alcohol radicles. This action is much less energetic than the corresponding action on the *nitrites*. The *nitrates* are not attacked in the cold by hy-

driodic acid of sufficient strength to decompose the *nitrites* instantly. On boiling, however, the *nitrates* are pretty easily attacked, nitrate of methyl much more readily than the corresponding ethyl-compound. The products in both instances are nitric oxide, ammonia, and an iodide of the corresponding alcohol radicle.

XIV.—*Titration of the Compound Ethers.*

By J. Alfred Wanklyn, Professor of Chemistry at the London Institution.

A close agreement between the results of an elementary analysis and the theoretical percentages of carbon and hydrogen required by a compound is often but a poor guarantee of the purity of that compound.

Pure acetic ether and acetic ether mixed with as much as 10 per cent. of common alcohol, would give very nearly the same results on combustion. For 10 per cent. of alcohol the difference in percentage is 0·23 of carbon, and 0·4 of hydrogen.

There is a similar difficulty in detecting amylic alcohol in acetate of amyl by means of a combustion. Pure acetate of amyl, and acetate of amyl contaminated with 10 per cent. of amylic alcohol differ in percentage by only 0·37 in the carbon, and 0·28 in the hydrogen. Indeed it seems that this very case has actually occurred in practice. The boiling point of acetate of amyl used to be given at 133° C. In reality, as I showed some time ago, the true boiling-point of the pure acetate is 140° C.—a result which has been recently confirmed by other experimenters, both in this country and in France.

Having had occasion to prepare a number of the compound ethers in a high state of purity, I have employed a titration as the test of purity, and have found it to be both rapid and easy of execution, and precise in its results. Berthelot has also, as is well known, employed a titration-method in some of his researches on the ethers.

The method of proceeding which I have employed is very simple. I take an alcoholic solution of caustic potash, and having determined the strength of it by means of standard acid, digest the ether, which I wish to titrate, with a given volume of this solution of potash. When the ether has been

decomposed by the potash, I determine the residual potash still unused by the ether. The difference between the potash originally caustic in the volume of solution, and the potash found caustic after digestion with the ether, is the quantity of potash neutralised by the ether.

The strength of the standard sulphuric acid which I use is about 4 per cent., and the alcoholic solution of potash about 6 per cent. I believe, however, that a higher degree of accuracy would be attainable by having the solution still stronger.

The standard sulphuric acid was made by diluting pure sulphuric acid with water, and afterwards determining the strength of the dilute acid by precipitation with chloride of barium. The standard acid was also verified with pure carbonate of soda, and with oxalic acid. A burette which had been carefully calibrated was used for measuring out the standard acid.

The alcoholic solution of potash was prepared by dissolving potash in pure alcohol of about 85 per cent. Experiments showed that neither a fortnight's keeping in a stoppered bottle, nor a short digestion at 100° C., altered its strength. The quantity of alcoholic solution of potash taken for a titration was measured in a small flask with a very narrow neck, on which a mark had been made with a file. The temperature of the potash-solution was observed. The capacity of the measuring flask up to the file-mark was about 50 cubic centimetres.

The digestion of the weighed quantity of ether with the alcoholic potash is managed in a flask with a long neck. In general, the compound ethers decompose with great ease and rapidity; if necessary, they might be sealed up in a digestion-tube and heated in the water-bath. All the examples about to be given are examples in which the digestion was managed without the employment of sealed tubes. The complete disappearance of the smell of the compound ether is, in many cases, a good criterion of the termination of the decomposition by the potash.

In titrating the solutions with the standard acid, a peculiar method of reading the point of neutrality was followed.

When sulphuric acid is added gradually to an alkaline solution, the following changes in the action on litmus paper are observable:—At first the colour with litmus is blue. By-and-bye the blue colour fades, and then, on adding another drop of dilute sulphuric acid, the colour is distinctly red. Now, in read-

ing off the quantity of standard sulphuric acid necessary for saturation, several plans may be taken. The utmost point at which litmus-paper remains distinctly blue may be read, and the earliest point at which a distinct red appears, may be read. The mean between these two points may then be marked down as the required point of neutrality. The utmost point at which a distinctly alkaline reaction is preserved may be marked down, or the earliest point of distinct redness may be taken. Of these three methods, I prefer the second for titrations involving organic acids, and have employed it in the following examples:

In determining the quantity of standard sulphuric acid necessary to neutralize the volume of alcoholic potash, I have read off the utmost point of distinctly alkaline reaction, and in afterwards reading off the quantity of acid required to neutralize the *residual* potash, I have also read off the utmost point of distinctly alkaline reaction. By this device the difficulty of the exceedingly faint acid reaction of the organic acids is eluded.

Benzoate of Ethyl.

I. 6·166 grm. taken; volume of alcoholic potash neutralised 62·1 c. c. of standard acid; residual potash, after the action of the ether, neutralised 10·2 c. c. of standard acid; 1 c. c. of standard acid corresponds to 0·03062 grm. of potassium. From these data, 100 grm. of benzoic ether neutralise 25·77 grm. of potassium.

II. 4·1580 grm. of benzoic ether taken; result, 100 grm. of benzoic ether neutralise 25·78 grm. of potassium. Theory requires 26·06 grm. of potassium.

Butyrate of Ethyl.—I. Ether taken = 2·020 grm.; result, 100 grm. neutralise 34·10 grm. potassium. II. Ether taken = 2·009 grm.; result, 100 grm. neutralise 33·98 grm. potassium. Theory requires 33·70 grm. potassium.

Valerianate of Ethyl.—I. 3·4530 grm. taken; result, 100 grm. neutralise 30·15 grm. potassium. II. 2·5181 grm. taken; result, 100 grm. neutralise 30·77 grm. potassium. Theory requires 30·08 grm. potassium.

Diethoxalate of Ethyl.—$\left\{\begin{matrix}CO(C_2H_5O)\\C(C_2H_5)(C_2H_5)(HO)\end{matrix}\right.$.—2·7580 grm. taken; result, 100 grm. neutralise 24·20 grm. potassium. Theory requires 24·44 grm. of potassium.

ERRATA.

Page line
138 12 *for* $C_4H_4Pb''_2O_6 . Pb''_2O$ *read* $C_4H_4Pb''O^6 . Pb''O$.

157 16 from bottom, *for* $\left.\begin{matrix}C_2H_2\end{matrix}\right\}O_2$ *read* $\left.\begin{matrix}C_2H_2\\H_2\end{matrix}\right\}O_2$

XV.—*Quantitative Analysis by "Limited" Oxidation. Examples. Lactic Acid and Diethoxalic Acid.*

By Ernest T. Chapman and Miles H. Smith.

It was shown on a former occasion* that the products obtained when organic bodies are gently oxidized, are the representatives of the radicals contained in the bodies operated upon. It was also shown that the fatty acids are unattackable by a solution containing eight per cent. of bichromate of potash and a suitable quantity of sulphuric acid.

It is possible to effect this gentle or limited oxidation in a precise manner, and in point of fact, to make accurate quantitative analyses of organic substances by employing it.

The following research affords an example of quantitative analysis made by the process of gentle oxidation.

Many years ago Liebig showed that lactic acid, when treated with binoxide of manganese and dilute sulphuric acid, yields carbonic acid and aldehyde. With bichromate of potash and dilute sulphuric acid, the results are the same. We have determined the amount of carbonic acid liberated by a definite quantity of lactic acid, when treated with bichromate of potash and sulphuric acid. With this object, lactate of baryta was formed. A weighed quantity of it was oxidized, and the carbonic acid thereby liberated was determined. Repeated determinations were made with the view of ascertaining the most accurate method of making these estimations. The apparatus finally adopted was as follows:—A flask, which had a tube joined on to its neck, was connected with a Will and Varrentrapp's nitrogen-apparatus containing concentrated sulphuric acid. This again was connected with a Liebig's bulb-apparatus, charged with potash, and this, in its turn, with a small tube filled with lumps of caustic potash. The neck of the flask was closed by a perforated cork through which passed the stem of a stop-cock bulb-tube. The nitrogen apparatus containing sulphuric acid was surrounded with cold water. To use the

* Chapman and Thorp, Chem. Soc. J., Dec., 1866 [2], iv, 477, "On the relation between the products of gradual oxidation, and the molecular constitution of the bodies oxidized."

apparatus, the potash-bulbs and their accompanying potash tube are first carefully weighed and then connected with the apparatus. A known weight of the lactate or other substance is introduced into the flask, which is then closed with the cork, and stop-cock bulb-tube. About 150 c.c. of 10 per cent. bichromate solution* are then poured into the apparatus through the bulb-tube, the stop-cock turned off, and the contents of the flask heated in the water-bath. A gentle continuous evolution of carbonic acid takes place; this of course bubbles through the sulphuric acid, and is absorbed by the potash. In the course of twenty minutes or so, the potash begins to be sucked back into the large bulb of the potash-apparatus exactly as in a combustion. When no more bubbles pass through the sulphuric acid, the water-bath is removed, and as soon as air begins to be drawn through the potash-apparatus the stop-cock of the funnel tube is opened, and air drawn through the apparatus by means of an india-rubber tube attached to the potash bulbs. The bulbs are then detached and re-weighed. The difference in weight of course gives the amount of carbonic acid which the substance has evolved. Slight deviations from the method here described have generally entailed great falling off in accuracy. Thus:—if the sulphuric acid be not surrounded by cold water, the violence of its action on the aldehyde, &c., is so great, that a little sulphurous acid is liberated. This also happens if the flask be boiled instead of being heated in the water-bath. The absorbent action of the sulphuric acid upon the steam causes so high a temperature, in spite of the cold water, that the aldehyde decomposes it, and an increase in weight in the potash-bulbs is the result. If, to avoid these evils, chloride of calcium be substituted for sulphuric acid, a portion of the aldehyde passes into the potash bulbs, thereby occasioning an increase in their weight. But if the method we describe be adopted, the results are almost as accurate as those of a combustion.

A ·9042 lactate of baryta gave ·2574 CO_2.
B 1·0242 „ „ „ ·2880 „

Calculating from these data we find that the lactate has furnished the following percentages of carbon, as carbonic acid.

* 100 grammes of bichromate, and 125 of sulphuric acid, introduced into a litre measure, and the measure filled up with water.

A	B	Theoretical percentage.
7·76	7·69	7·62

Under "theoretical percentage" we have placed one-third of the total carbon of the compound. The other two-thirds of the carbon are converted first into aldehyde, and then into acetic acid. This is proved by digesting a known weight of lactate of baryta with a mixture of bichromate of potash and dilute sulphuric acid (10 per cent. solution)* in a sealed tube for about $1\frac{1}{2}$ hours at 100° C. On opening the tube, gas escaped, but no smell of aldehyde could be detected. The contents of the tube were transferred to a small flask and treated with zinc and sulphuric acid. The object of this treatment was to reduce the chromic acid, and thereby prevent its having any action during the subsequent distillation. The flask was connected with a Liebig's condenser, and its contents distilled to dryness. Water was then added to the residue in the flask, and this also distilled to dryness. The two distillates were mixed, the condenser washed out, and the washing added. The distillate was then treated with carbonate of baryta and boiled for some time in a flask. The baryta-salts so obtained were filtered from the excess of carbonate, the latter well washed and the washings added to the filtrate. This latter was evaporated to a small bulk, and then filtered from a little carbonate of baryta which had separated, the filter and carbonate being both well washed, and the washings added to the filtrate which could now contain nothing but soluble baryta-salts. It was evaporated to dryness, dried at 150° C., and weighed.

Treated in this way 1·0166 grammes of lactate of baryta yielded ·8198 grammes of the new baryta-salt or 80·64 per cent. Theoretically, it should yield 80·95 per cent. A portion of this salt was tested for formic acid, but this acid was absent.

In another portion the percentage of barium was determined ·5352 of substance yielded· 4892 Ba_2SO_4: percentage of barium 53·70. Acetate contains 53·726.

Now, as the general formula of the acids of the acetic series is $(CH_2)_nO_2$, and as this formula holds good, not only for any one of these acids, but also for any mixture of them, it follows that, if we can determine the amount of oxygen in such a mix-

* When we speak of a solution of such a percentage, we always refer to the bichromate of potash, not to the chromic acid.

ture of acids, and subtract it from the weight of the acids, or acid, the remainder will have the composition CH_2. We cannot however directly determine the oxygen; but all the acids of this series contain one eq. of replaceable hydrogen. Now this can be determined with the greatest ease. It is only necessary to convert the acids into salts, and then determine the amount of base. The baryta-salt is one of the best to employ for this purpose, because in this case the base can be determined very rapidly, and the salts themselves can be obtained easily in a state of perfect dryness and neutrality.

Taking the above example, we find that 100 parts of lactate of baryta yield 80·64 of baryta-salt of the acids of the acetic series. These 80·64 parts contain 53·70 per cent. of barium, or $\frac{80{\cdot}64 \times 53{\cdot}70}{100} = 43{\cdot}304$ parts of barium. If 43·304 represent one eq. barium, ·632 will represent one eq. hydrogen and 20·23 two eq. oxygen. Subtracting the barium and oxygen from the total baryta-salts and adding the hydrogen, we obtain the amount of CH_2. $80{\cdot}64-(43{\cdot}304 + 20{\cdot}23) + {\cdot}632 = 17{\cdot}738$. Now, CH_2 contains $\frac{6}{7}$ths of its weight of carbon, which is, therefore, $\frac{17{\cdot}738\ CH_2 \times 6}{7} = 15{\cdot}21$. This number represents the percentage of carbon existing in the acetous form in the lactate. This result confirms the formula for lactic acid proposed by Frankland and Duppa. They regard this substance as oxalic acid in which one atom of oxygen has been replaced by methyl and hydrogen.

Oxalic acid.	Lactic, or hydromethoxalic acid.
$\left\{\begin{matrix}COHO \\ COHO\end{matrix}\right.$	$\left\{\begin{matrix}C(CH_3H)HO \\ COHO\end{matrix}\right.$

Analysis of Lactate of Baryta.

	Found. I.	Found. II.	Found. III.	Theory.
Carbon existing as oxatyl	7·76	7·69	—	7·62
Carbon existing in the acetous form	—	—	15·21	15·24

With the concurrence of Messrs. Frankland and Duppa, we have studied the action of the chromic solution on diethoxalic acid.

We have effected an improvement in the preparation of the diethoxalate, whereby much time is saved, and a somewhat larger yield obtained. We employ freshly granulated zinc, granulated as finely as possible, and the mixture of iodide of ethyl and oxalate of ethyl, in the same proportions as those given by Frankland and Duppa; but in addition to this, we add a small quantity of mixed zinc-ethyl and ether. The zinc is dried on the sand-bath, and introduced into a flask large enough to contain about three times the volume of the liquid to be operated upon. The mixed ethers, which have been very carefully dried, are poured on the zinc while it is still so hot, that the first portion boils on coming in contact with it. The mixture of zinc-ethyl and ether is then added and the flask at once placed in the cold water-bath and connected with an inverted Liebig's condenser. The water-bath, containing but little water, is then slowly heated till the mixed ethers begin to drop back, by which time the action will have started. The water is then syphoned off. In three preparations made in this way we have never found the reaction get too brisk. In about an hour and a half the reaction almost stops: it is completed by heating in the water-bath. When the flask is somewhat cool though not cold, as much tepid water is added as will allow of the contents of the flask being well shaken up together. The water, and as much of the solid matter as can be easily removed with it, are transferred to a wide-mouthed tin can. More tepid water is added to the residue in the flask and in this way the whole contents of the flask are transferred to the tin can. The can is then heated over the naked flame. The distillate generally divides into three layers. We add about 40 c.c. of ether to it, and shake if up. The top and bottom layers unite and can easily be decanted from the watery part. After the oily layer has been decanted, it is distilled and that portion of it which comes over below 120° is again agitated with the watery part. It is again separated and treated in the same manner as before. Three of four such operations are enough to obtain almost all the diethoxalic ether. The fraction of higher boiling point is then dried and fractionally distilled, when most of it is found to boil at 175° C. There is only a very small quantity of liquid of higher boiling point, not more than a drop or so. We subjoin the details of four operations:—

1st. 600 grm. of mixed ethers (iodide of ethyl 409 grm.

oxalate of ethyl 191 grm.), treated as directed by Frankland and Duppa, yielded 82 grm. of the pure ether; the digestion lasted 15 hours. (The yield obtained by them and mentioned in their paper is almost the same, viz., 86 grm. from the same mixture.)

2nd. Same quantities treated as described above with only three grm. of mixed zinc-ethyl and ether (containing about 30 % of the former) yielded 91 grm. Digestion lasted about 5 hours.

3rd. Same quantities, about 15 grm. of the mixed zinc-ethyl and ether being added, yielded 109 grm. Digestion lasted 2 hours.

4th. Same quantities + 65 grm. of ether and zinc-ethyl yielded 118 grm. Digestion lasted 2¼ hours.

Three parts of zinc-ethyl should theoretically yield about two of the ether. We will therefore subtract the amount of diethoxalate of ethyl which might have been produced by the zinc-ethyl, and then the results stand thus :—

1st operation	15 hours		no zinc-ethyl		yield	82 gr.
2nd	„	5	„	1 grm.	„	„	90 „
3rd	„	2	„	5	„	„	105⅔ „
4th	„	2¼	„	22¼	„	„	104 „

From this it would appear that a small quantity of zinc-ethyl greatly promotes the action, but that no advantage is gained by using a large quantity.

A very small trace of water impedes the action, even though there is more zinc-ethyl present than would decompose it. In fact, if the zinc be allowed to get cold, it becomes damp enough to delay the action, for, an operation in all respects resembling No. 3, but in which the zinc had been allowed to stand all night in the flask, the mouth of which was covered with paper, lasted 9 hours.

We have nothing to add to the account of the physical properties of this ether given by Frankland and Duppa. It has been titrated by Professor Wanklyn and 100 parts of the ether neutralized an amount of potash-solution corresponding to 24·20 parts of potassium. Theory would require 24·44. It was therefore pure.

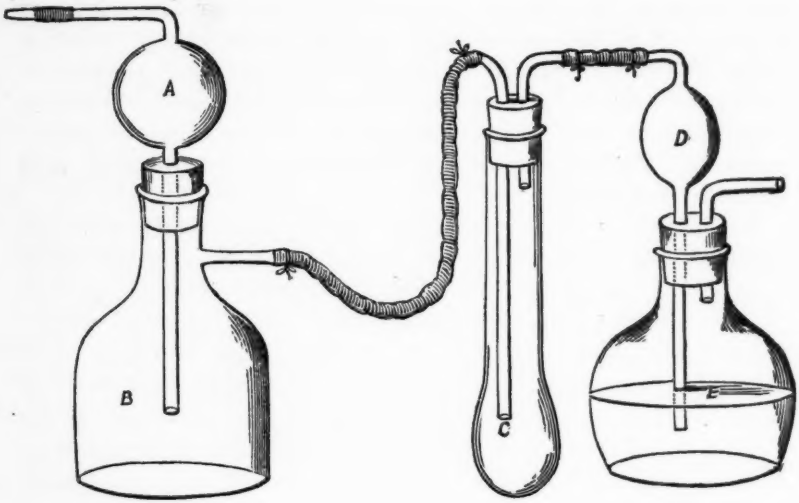
We prepared the acid by decomposing the ether with solution of caustic potash, both with and without alcohol. The products of both operations were evaporated down to a small bulk,

excess of dilute sulphuric acid added, and the mixture agitated with ether. The ether employed for this purpose should be free from alcohol for the reason given below. When the ether has become charged with the acid, it is decanted and dried over chloride of calcium. The ether is then for the most part distilled off in the water-bath, and the thick syrupy solution thus obtained is placed over sulphuric acid and allowed to stand some days. The product is a dry white mass of crystals consisting of pure diethoxalic acid. If the ether employed contained alcohol, the product would be contaminated with chloride of calcium.

When diethoxalic acid is treated with bichromate of potash and sulphuric acid, and the mixture gently warmed, a peculiar smell is produced and gas is evolved in abundance. This gas proved to be carbonic acid. A determination of its quantity would, we thought, throw light on the nature of the reaction. For this purpose we did not employ the same apparatus as that before described, because with the greatest care one is apt to lose many determinations from the sucking back becoming very violent, and also because with it we could only use small quantities.

In the apparatus about to be described, the carbonic acid is determined by loss. It will be readily understood by a reference to the figure on page 180. A is a large bulb pipette, one limb of which descends into the flask B, and the other is bent at right angles and closed by a piece of india-rubber tube containing a removable glass plug. The flask B has a tube let into the side of its neck. This tube is connected by a long india-rubber tube with a glass tube passing through the cork and descending almost to the bottom of the long-necked flask C. Another tube just passing through the same cork is connected with the pipette D, the long stem of which passes into the flask E. The cork of this flask has another aperture open to the air. E contains sulphuric acid. The point of D dips just so far into this acid that on sucking the air out of it, it cannot be completely filled by the acid. The flask C is empty. When the apparatus is in use C is surrounded by cold water. It serves to condense steam and the vapours of any organic liquids. B contains the substance to be operated upon, and A the bichromate solution. The total weight of the apparatus when charged is about 420 grammes. It is weighed upon a

balance capable of carrying a kilogramme, and also capable when loaded with 500 grammes in each pan, of indicating half a milligramme.



The pipette A was charged with bichromate solution by immersing its point in the liquid and sucking out the air. A known weight of diethoxalic acid was dissolved in water in B, the apparatus put together and weighed. The bichromate solution was then run into the flask by removing the glass plug. As soon as it had all run in, the plug was replaced, C immersed in cold water and B gently warmed. Carbonic acid was at once evolved. The evolution lasted about ten minutes. The contents of the flask were then boiled rather sharply, care being taken, however, not to overtask the condensing powers of C, in fact the top part of it continued cool during the whole operation. After a few minutes the boiling was discontinued, the glass plug removed, and a current of dry air forced through the apparatus. It was then cooled, air being allowed to enter which had been previously dried by passage through a chloride-of-calcium tube. The whole apparatus was then dried and transferred to the balance-case and allowed to remain there for an hour. It was then reweighed. The loss of weight of course indicated the amount of carbonic acid.

Weight of diethoxalic acid employed....	3·1375	grammes.
Weight of apparatus before the operation	419·153	„
„ „ after „	418·107	„
Weight of carbonic acid evolved	1·046	„

Therefore, percentage of carbon, 9·093. Diethoxalic acid contains 6 eqs. and 54·55 per cent. of carbon. By the proportion

$$54{\cdot}55 : 6 : : 9{\cdot}093 : x$$

$$x = 1{\cdot}0002,$$

we learn how many eqs. of carbon are evolved in the form of carbonic acid. According to the theory of its composition put forward by Frankland and Duppa, this substance contains 1 eq. of oxatyl, and should, therefore, liberate one-sixth of its carbon as carbonic acid.

$$\left\{\begin{matrix} C\begin{pmatrix} C_2H_5 \\ C_2H_5 \end{pmatrix} HO \\ COHO \end{matrix}\right. = C_6H_{12}O_3.$$

We have therefore shown that one equivalent or $\frac{1}{6}$th of the carbon has been liberated in the form of the characteristic oxidation-product of oxatyl, viz., carbonic acid. This in itself is a strong corroboration of the correctness of the above hypothesis.

At the end of the above operation, the flask C contained, in addition to water, about 2 c.c. of a slightly yellow, volatile, mobile, and fragrant liquid. A few grammes of diethoxalic acid, were heated in a small distilling flask with excess of bichromate of potash and sulphuric acid. In this way more of the same liquid was obtained. It was dried over chloride of calcium, and its boiling point taken. It boiled quite constantly at 101°, and had the peculiar smell of Wanklyn's propione. The next point was to determine how much of this liquid was produced. With this object 14·3 grm. of diethoxalic acid were introduced into a small retort, the neck of which was dipped under the surface of solution of caustic potash, contained in a small receiving flask. The object of the potash was to absorb the carbonic acid and thus prevent the loss which would have occurred had this gas escaped saturated with the vapour of organic liquid. Excess of the 10 per cent. bichromate solution was then added to the diethoxalic acid in the retort, and the whole gently warmed, and finally boiled. When about a tenth of the contents of the retort had distilled over, the operation was stopped, and the contents of the receiver saturated with carbonic acid, care being taken not to pass more carbonic acid

than was immediately absorbed. The oily layer floating on the surface was decanted and placed over chloride of calcium. The solution of carbonate of potash was partially distilled, and the distillate saturated with chloride of calcium, when a small quantity more of the oily liquid rose to the surface. This was decanted and added to the main product. When it was judged that the liquid was dry, it was distilled through a very small condenser into a tared flask and weighed. The weight was 9·40 grm. We had therefore obtained 65·7 per cent. of the weight of the diethoxalic acid in the form of this liquid. As proved below, the liquid is propione. We should theoretically have obtained 65·15 per cent. of it.* More of the substance was prepared without any special precaution being taken to collect the total product. Even under these circumstances the yield is from 58 to 60 per cent. of the diethoxalic acid employed. It is not, however, necessary to prepare diethoxalic acid. The ether need simply be decomposed with caustic potash, the alcohol distilled off, and the crude potash-salts so obtained treated directly with the oxidising mixture, when the propione may at once be distilled off. Carefully dried over chloride of calcium, this substance is colourless or faintly straw-coloured. It has a peculiar but very fragrant smell. It boils quite constantly at 101. Its specific gravity (water at 4° C. = 1) is at 0° C. ·8145, at 15° C. ·8015. It is not easily attacked by oxidising agents, as is indeed sufficiently apparent from the large yield obtained. When distilled with water, it all comes over with the first few drops, leaving the water quite tasteless. It is soluble in about 24 parts of water, much less so, however, in saline solutions. It appears to be quite insoluble in a saturated solution of chloride of calcium. It is of course miscible with alcohol and ether in all proportions. It was oxidised by prolonged digestion in a sealed tube with the 10 per cent. bichromate solution. 2·1848 grm. of the substance were digested with excess of the oxidising solution for 15 hours in the water-bath. The tube was then cooled and opened. No gas whatever escaped. The contents of the tube were transferred to a small distilling flask and treated precisely as described when speaking of the products of oxidation of lactic acid. The distillate was converted into baryta salts, and the salts dried at 150° C. and weighed. Weight 6·635 gram.

The percentage of barium in these barium-salts was deter-

* This slight excess was doubtless due to moisture.

mined by conversion into sulphate. 0·5421 of the substance gave 0·4720 Ba_2SO_4. Therefore the percentage of barium was 51·19. The remainder of the salt was dissolved in water. It did not form a perfectly clear solution. As it was intended to fractionate the acids in this salt, and as the baryta-salt is exceedingly inconvenient for this purpose, excess of sulphate of potassa was added, and as much standard sulphuric acid as would combine with about one-fourth of the barium. Of course the whole of the barium was precipitated as sulphate and the acids were obtained in the form of potash-salts and free acid. They were filtered from the sulphate of baryta and the free acid distilled off. The remainder of the salts were fractionated in the manner described in a former paper,* with the following results:—

Substance taken.	Ba_2SO_4 found.	Per cent. Ba found.	Theoretical per cent. Ba.	Salt to which this corresponds.
1st fraction ·3732	·3082	48·56	48·41	Propionate
„ „ ·4001	·3288	48·32	—	—
2nd „ ·5199	·4451	50·34	Intermediate	Mixture
3rd „ ·3589	·3170	51·94	—	—
„ „ ·6290	·5558	51·96	—	—
4th „ ·4201	·3845	53·81	53·726	Acetate

From the first fraction in the foregoing table, it appears that propionic acid is one of the products; from fractions 2 and 3, that no acids higher in the series than propionic acid are present; finally, from fraction 4 that acetic acid is present. This fractionation, taken in conjunction with the fact that the percentage of barium from the mixed salts is very close to that required by a mixture of acetate and propionate of baryta in equivalent proportions, justifies us in assuming that the mixed salts really had this composition. The theoretical percentage of barium in the mixture $C_2H_3BaO_2$ + $C_3H_5BaO_2$ is 50·93. We obtained 51·19. The total amount of the mixed salts obtained was 97 per cent. of the theoretical quantity, calculated on the assumptions that the above is the formula of the mixed salt, and that one eq. of propione yields on oxidation one eq. of acetic and one eq. of propionic acid. However the above experiment had not been conducted absolutely without loss. It was therefore repeated with the greatest possible care upon a smaller quantity of propione.

* Chapman and Thorp, Chem. Soc. J., Dec., 1866.

Digested in the water-bath with the chromic solution for eight hours, and treated precisely in the same manner as in the estimation of acetic acid in the lactate, ·4362 of propione yielded 1·3542 of mixed salts or 99·28 per cent. of the theoretical quantity. A portion of these salts was carefully tested for formic acid, which was absent. In another portion the percentage of barium was determined. ·4908 of the mixed salts yielded ·4252 of sulphate of baryta, therefore 50·94 per cent. of Ba. As above remarked the theoretical percentage for these mixed salts is 50·93.

Calculating from these data in the manner previously described, we find that 100 parts of propione have yielded 310·5 of the mixed salts. As these salts contain 50·94 per cent. of Ba, we have to subtract this percentage from them, (that is to say 158·14) and to add to them an amount of hydrogen equivalent to this amount of barium, and also to subtract twice the equivalent amount of oxygen; the remainder will be, as already proved CH_2.

Amount of mixed salts	310·5
Amount of H. eq. to Ba.....	2·31
	312·81
$Ba + O_2 =$	232·03
Amount of CH_2	80·78
$\frac{CH_2 \times 6}{7} = C$.....	69·24

According to our oxidation, therefore propione contains 69·24 of carbon. By calculation it should contain 69·76. We are perfectly confident that with care even a better result might have been obtained.

The next thing to be determined was the amount of oxygen required to effect this oxidation. This result was approximately obtained by precipitating the sesquioxide of chromium which had been reduced from chromic acid by the action of a known weight of propione. We say approximately because the estimation is attended with some little difficulty. In the first place ammonia is inadmissible as a precipitant, because it would precipitate not only the sesquioxide of chromium, but also some chromate of chromium. We are therefore compelled to use

potash, but potash adheres so tenaciously to the sesquioxide, that it is practically impossible to remove it by washing.

·3435 of propione was digested for ten hours with 46 c.c. of the standard chromic solution. The tube was then cooled and opened. No gas was evolved. The contents were transferred to a dish, boiled, and excess of caustic potash added. The precipitate produced was pure pale green. It was washed, first by decantation, and then on the filter, until the washings did not in any way affect neutral nitrate of silver, did not change the colour of litmus, and left no appreciable residue on evaporation. The precipitate was then dried, ignited, and weighed. Weight ·6668. On treating this with water, some chromate dissolved. The whole contents of the crucible were boiled with strong hydrochloric acid and a little alcohol. Ammonia was then added and the fluid again boiled. The precipitate was then filtered off, washed, dried, ignited, and weighed. Weight ·6332. This precipitate, on treatment with water, again coloured it yellow, thereby showing that it still contained chromate. The amount was however very small. The latter number is therefore assumed to have been very nearly the true weight of the sesquioxide. Calculating from these data, we find that 100 parts of propione had required 57·83 parts of oxygen to convert it into acetic and propionic acids. Calculating from the data given on a previous page, we find that 100 of propione yielded 154·7 of the mixed propionic and acetic acids. Now these acids would contain 73·14 of oxygen. But the amount of oxygen employed was 57·83; therefore the propione must have contained oxygen. On subtracting one of these numbers from the other, we obtain 15·31 as the amount of oxygen contained in propione. The theoretical quantity would be 18·6. This number, wide as it is of the mark, proves distinctly that acrylic acid is not among the oxidation-products of propione; for if it were, we should have required a far higher percentage of oxygen than 57·83 to oxidize propione. The theoretical quantity is 55·8. The quantity required if acrylic acid were produced would be 74·4. From the nature and amount of the acids obtained it is evident that propione contains 5 eqs. of carbon.

From the relation subsisting between the amount of acids, and the amount of oxygen required to produce them, it is evident that the propione requires 3 eqs. of oxygen to convert it into acids of the acetic series. It is further evident that the

propione can have lost no hydrogen during its oxidation. Had it done so, more oxygen would have been required to oxidize it. Such being the case it is evident that the amount of hydrogen found in the form of the acids of the acetic series, is the total amount contained in the compound. We therefore subjoin a comparative statement of the composition of propione as determined by a careful combustion, by limited oxidation, and by calculation.

	Combustion. I.	Limited oxidation.	Calculation.
C_5.....	69·58	69·24	69·76
H_{10}	—	11·49	11·63
O.....	—	—	18·61
			100·00

I. ·1662 grammes of propione burnt with chromate of lead gave ·424 grammes CO_2.

The foregoing analytical results relating to diethoxalic acid, are collected and exhibited in a tabular form in the following statement:

Oxidation of diethoxalic to water, carbonic acid and propione thus:—

$$\left\{\begin{matrix}C(C_2H_5)_2(HO)\\CO(HO)\end{matrix}\right. + O = H_2O + CO_2 + C(C_2H_5)_2O.$$

100 parts of diethoxalic acid gave 33·37 parts of carbonic acid. Theory 33·33.

100 parts of diethoxalic acid gave 65·7 parts of propione (weighed as propione). Theory 65·15.

Oxidation of propionic to propione and acetic acids, thus:—

$$\overset{\text{Propione.}}{C(C_2H_5)_2O} + O_3 = C_3H_6O_2 + C_2H_4O_2.$$

100 parts of propione gave 310·45 parts of baryta-salts (propionate and acetate). Theory 312·8.

The percentage of barium found in the mixed baryta-salt was 50·94. Theory 50·93.

A satisfactory separation of the propionic and acetic acids was made, and it was proved that no other acid was present.

From these data we give the following analysis of diethoxalic acid.

	Found.	Theory.
Carbon existing as oxatyl, weighed in the form of CO_2	9·10	9·09
Carbon existing in the propylic form, weighed as propionate of baryta	27·29	27·27
Carbon existing in the ethylic form, weighed as acetate of baryta	18·20	18·18

We conclude that were any chemist called on to deduce the formula of diethoxalic acid from the data given above, he could only arrive at a formula practically identical with that proposed by Frankland and Duppa from synthetical evidence.

Laboratory of the London Institution.

XVI.—*On the Preparation of Berberine from Coscinium Fenestratum.*

By John Stenhouse, LL.D., F.R.S., &c.

The plant *Coscinium fenestratium* belonging to the natural order *Menispermaceæ*, is a large rope vine and is very abundant in the forests of Ceylon and other parts of India. As is well known, berberine was extracted from it by Mr. J. D. Perrins, many years ago,* and I find that when treated by the following process, it yields from 1½ to 3½ per cent. of pure berberine, according to the quality of the wood, which probably depends very much on the season at which it is collected.

One part of acetate of lead is dissolved in 3 parts water, and to the boiling solution 1 part of very finely ground litharge is added in small portions, and heated until the whole forms a thick pasty mass; 20 parts of the finely ground columbo wood (*coc. fen.*) is boiled with the subacetate of lead thus obtained previously diluted with 100 parts of water. After about three hours' digestion, the mixture is strained through a bag-filter and the partially exhausted wood is heated twice with the same quantity of water, these weak liquors being used instead of water in the extraction of fresh quantities of wood. The first and strongest liquor (after adding a little finely powdered litharge) is concentrated until, on cooling, berberine crystallises out in dark brown tufts of needles. The mother-liquor from

* Phil. Mag. [4], iv, 99.

these crystals is strongly acidulated with nitric acid and allowed to stand for 24 hours, when the remainder of the berberine present is precipitated as nitrate, which is very insoluble in solutions containing a slight excess of nitric acid.

The nitrate thus obtained may be converted into berberine by boiling with about 10 times its weight of water, adding an excess of ammonia and allowing it to cool; but it is more advantageous to substitute hydrate of calcium for the ammonia in decomposing the nitrate, as berberine does not seem to be acted upon, even by long boiling with hydrate of calcium, whereas ammonia, potassa, and soda all decompose it more or less, with formation of a dark brown substance.

In order to purify the crude berberine obtained by the above process, it is dissolved in boiling water, and subacetate of lead added as long as any precipitate is produced. This solution, filtered whilst hot, almost solidifies on cooling to a mass of yellow needles, which however still contain lead and organic impurities. They are collected on a cloth filter, pressed, dissolved in boiling water, and sulphuretted hydrogen passed through it. The hot solution, after filtration to separate the precipitated sulphide of lead, which carries down some organic impurities, is acidulated with acetic acid, and allowed to cool. The bright yellow needles of nearly pure berberine are collected, pressed, and dried at a gentle heat. If required quite pure, they may readily be obtained so by one or two recrystallisations from boiling water. Berberine is insoluble in benzol and bisulphide of carbon. The berberine in this wood seems to be combined with an organic acid, forming a salt soluble with difficulty even in boiling water. So that by treating the wood with water alone, a clear yellowish brown solution is obtained which becomes turbid and opaque on cooling; if this be now precipitated by subacetate of lead and evaporated, it yields but a very small amount of berberine for the quantity of water employed. By boiling the wood, however, with subacetate of lead, almost the whole of the berberine is at once extracted. This process of boiling with subacetate of lead will no doubt be found equally applicable to the extraction of berberine from any of the other plants in which it is found.

Theine.—I have successfully applied the above process to the extraction of theine from tea.

XVII.—*On the Amount of Carbonic Acid contained in Sea-Air.*

By T. E. Thorpe, Dalton Scholar in the Laboratory of Owens College, Manchester.

The existence of carbonic acid in the air of the land was first demonstrated by Macbride,* of Dublin, so far back as 1764, but its invariable presence in the atmosphere of the sea was not proved by experiment until 1836.

The experiments of Saussure, Boussingault, Angus Smith, and others, furnish exact knowledge concerning the distribution of the carbonic acid contained in the air of the land, together with the causes and limits of its variations due to differing circumstances of situation and weather: determinations of its amount in the air over the sea under, as far as possible, similar conditions are alone wanting to render the history of this particular constituent of our atmosphere tolerably complete.

In his well known memoir on the carbonic acid of the atmosphere, the younger Saussure† clearly showed the influence which large bodies of water exert on the proportion of this gas in the air. Thus from simultaneous observations he found that air taken near the middle of the Lake of Geneva contained on the average slightly less carbonic acid than the air of the land taken at a short distance from the bank, the ratio of the amounts of carbonic acid at the two stations being as 95 to 100. This abstraction of carbonic acid by the waters of the lake, might, with all probability, have been foreseen, in fact Vogel‡ had previously obtained a similar result and deduced a like conclusion from a comparison of the turbidities produced in baryta-water by the air of the Channel and of Dieppe. To such an extent was this action supposed to occur that it was formerly believed the air over the open sea would be found to contain absolutely no carbonic acid; indeed Krüger§ was unable to detect its presence over the Baltic; Emmet and Dalton,‖ however, thirty years ago, conclusively showed that it is invariably present even in the air of mid-ocean.

* Experimental Essays, 1764.
† Ann. Ch. Phys., xliv, 1830.
‡ Ann. Phil., N. S., vi, 75.
§ Schw. J. xxxv, 379.
‖ Phil. Mag. [4], xi, 225.

The only series of determinations hitherto published of the amount of carbonic acid contained in the air above the ocean are those of Lewy.* At the request of the French Academy Lewy, in 1848, collected the air of the Atlantic at different times during a voyage from Havre to Santa Marta, and determined the proportion of its three principal constituents in the eudiometric apparatus of Regnault and Reiset.

The following table shows the results of these determinations :—

TABLE I.

Lewy's Analyses of the Air of the Atlantic Ocean.

Dec. 1847.	Hour.	Temp. of Air.	Temp. of Sea.	Wind.	Sky.	Lat. N.	Long. W. of Paris.	Distance from Continent.	Each result the mean of three analyses.			
									CO_2.	Oxygen.	Nitrogen.	
		°C.	°			° ′	° ′	leagues				
1st	11.30 a.m.	16·0	—	E.S.E.	Cloudy	47·30	10·5	55	4·881	2105·170	7889·949	Left Havre on Nov. 25th. Weather continued wet whilst in the Channel.
4th	3.0 a.m.	13·0	—	N.W.	Unclouded	47·00	13·0	120	3·388	2096·321	7900·341	
8th	12.15 p.m.	17·5	18·6	N.E.	Few clouds	35·40	20·35	190	5·497	2105·945	7888·558	54 leagues from Madeira.
17th	3.0 p.m.	23·0	23·8	do.	Unclouded	22·5	39·0	400	5·771	2106·030	7888·199	30 leagues south of the tropics.
18th	3.0 a.m.	21·5	—	E.	do.	21·45	41·3	435	3·346	2096·139	7900·515	Midway between Africa and America. Sea very phosphorescent.
18th	3.0 p.m.	24·0	24·5	do.	Few clouds	21·9	42·25	412	5·420	2106·099	7888·481	
19th	3.0 a.m	2·.0	—	do.	Unclouded	20·35	43·35	390	3·388	2096·074	7900·538	Sea very phosphorescent.
26th	1.0 p.m.	27 2	27·0	do.	do.	15·49	64·28	80	5·288	2105·889	7888·823	18 leagues from Martinique
28th	2.15 p.m.	27·0	27·2	do.	do.	14·6	70·4	60	5·093	2105·686	7889·221	45 leagues from Curaçoa.
30th	12.30 p.m.	25 5	25·5	N.E.	do.	12·5	76·0	15	5·143	2105·789	7889·068	15 leagues from Santa Marta.
31st	3.0 a.m.	24 0	—	E.	do.	—	—	1 to 2	3·767	2101·114	7885·119	Entering the port of Santa Marta.

The mean composition of the air of the Atlantic, from these analyses, is therefore in 10,000 volumes :—

Carbonic acid	4·630
Oxygen.....	2102·750
Nitrogen	7892·620
	10000·000

These numbers differ but slightly from those usually given as representing the average composition of the atmosphere of

* Ann. Ch. Phys. [3], xxxiv, 5.

the land. On examining the experimental details, however, it appears that the air of the day was found to be considerably richer in carbonic acid and oxygen than the air of the night. The following are the means of each series :—

	The day. (7 experiments.)	The night. (4 experiments).
Carbonic acid	5·299	3·459
Oxygen	2105·801	2097·412

This remarkable difference appeared to become greater as the middle of the ocean was approached, where the air of the sea was less liable to be mixed with that of the land. The means of the analyses of air collected by Lewy, at about equal distances from the continents at the same hours, night and morning, of the same day, and under similar meteorological conditions, are as follows :—

	At 3 a.m.	At 3 p.m.
Carbonic acid	3·346	5·420
Oxygen	2096·139	2106·099

or a difference in 10,000 volumes of air of 2·074 in the carbonic acid, and 9·960 in the oxygen.

These singular diurnal variations in the composition of the atmosphere of the sea are ascribed by Lewy to the evolution and consequent admixture with the superincumbent air, during the daytime, of dissolved gases from the heated surface-layers of the sea, such gases being considerably richer, as is well known, in oxygen and carbonic acid than ordinary air. During the night, on the other hand, this disengagement of gas is supposed to be arrested. Morren,* and subsequently Lewy,† have shown that the changes in the relative amounts of the several gases held in solution in sea-water depend :—(1) upon the variations in intensity of direct and diffused solar light, producing a corresponding effect upon the vitality of sea-plants and animals; and (2) upon the alterations of temperature affecting the relative amounts of these dissolved gases in accordance with the known laws of gaseous absorption. Consequently if such causes can at all influence the composition of the atmosphere of the sea, it is reasonable to expect that the variations would be most perceptible in the air above the

* Ann. Ch. Phys. [3], xii, 5. † Ann. Ch. Phys. [3]. xvii, 5.

tropical oceans, in whose tepid waters infusoria exist in enormous quantities, and where the intensity of total sunlight is very great, and its changes exceedingly rapid.

It would thus appear from Lewy's experiments that the mean quantity of carbonic acid in the air above the ocean is sensibly greater than in the air of the land, and that, contrary to the statements of Vogel and Krüger, sea-water does not abstract the carbonic acid from the air, but even causes a sensible increase in its comparative amount. Considering the difficulty generally experienced in accurately measuring in the eudiometer contractions so minute as the absorption of the carbonic acid from a small volume of atmospheric air, it appeared desirable to test the validity of the above conclusions by a series of experiments made by one of the more convenient and accurate methods which we now possess for the estimation of atmospheric carbonic acid.

In a paper read before the Literary and Philosophical Society of Manchester,* I communicated the results of a series of determinations of the amount of carbonic acid contained in the air over the Irish Sea. The following contains, in addition to these, the results of a more extended inquiry on the air over the Atlantic Ocean. All these determinations were made by Pettenkofer's method,† according to which the amount of atmospheric carbonic acid can be estimated with far greater accuracy than by any eudiometric method hitherto described. It consists in absorbing the carbonic acid from a known volume of air by means of baryta-water, free from alkalies and of known strength, the amount of carbonic acid so absorbed being ascertained by the difference in the amounts of standard acid required for the exact neutralisation of the baryta-water before and after the absorption. Any weak acid which is not volatile at ordinary temperatures may be employed for this purpose; but oxalic acid is preferable for obvious reasons, the only objection to its use being that its solution requires to be often prepared anew, since it is apt to decompose when kept for any great length of time. The solution of oxalic acid used for these experiments was made so that one cubic centimetre corresponded to one milligramme of carbonic acid: it thus contained 2·864 grammes of pure crystallised oxalic acid per litre. Twenty-five cubic centimetres of the baryta-solution

* Mem. Lit. Phil. Soc. [3], vol. iv. † Chem. Soc. Qu. J., x, 292.

were originally made to correspond to about twenty-eight or thirty of oxalic acid, but of course the exact strength was known previous to each experiment. The bottles were generally filled with the air by means of the bellows-pump, but sometimes when the wind was strong it sufficed to hold them up for a minute or two in such a manner that the air could circulate freely within. After the admission of the baryta-water the bottles were closed by metallic caps, provided with a caoutchouc flange, fitting air-tight to the necks. The baryta-water remained in contact with the enclosed air for about an hour, during which time the bottles were frequently agitated. Although even this is longer than experience has shown to be actually required for the complete absorption of the carbonic acid, still in several of the experiments the bottles were allowed to stand for three, four, or even six hours before the solutions were titrated. Fifty cubic centimetres of baryta-water were employed in every case to absorb the carbonic acid, of which twenty-five were afterwards withdrawn to determine the amount so neutralised. A Mohr's burette was used, for which a table of capacity had been previously constructed by weighing and interpolating in the ordinary way.

From the data thus obtained the volume of carbonic acid in 10,000 volumes of air is easily calculated by means of the following formula, in which p represents the difference between the amounts of oxalic acid required for exact neutralisation before and after the absorption, or, since one cubic centimetre of the oxalic acid solution corresponds to one milligramme of the carbonic acid, the amount in milligrammes of the carbonic acid contained in the quantity of air experimented upon: V the capacity of the flask; v the volume of baryta-solution employed for absorption; H the observed height of the barometer; and t the observed temperature:—

$$\frac{p\,(1 + \cdot003667 \times t)760}{H(V-v)0\cdot0019714}.$$

The calculation of a large number of determinations is much facilitated by the use of a table showing the weights in grammes of a cubic centimetre of carbonic acid at different temperatures and pressures, and by employing a constant volume of baryta-solution in the experiment. If v' be the reduced volume of air, and w the weight in grammes of a cubic

centimetre of carbonic acid at the observed temperature and pressure, the formula becomes,

$$\frac{p}{v' \times w.}$$

The experiments on the air of the Irish Sea were, by the kind permission of the Honourable Board of Trinity House, made during the month of August, 1865, on board the "Bahama Bank" light-vessel, situated in lat. 54° 21′ N. and long. 4° 11′ W., seven miles W.N.W. of Ramsey, Isle of Man, and consequently nearly equidistant from the shores of England, Scotland, and Ireland. This ship is placed to mark the proximity of a dangerous bank, by which for the greater part of the day, a strong current setting in from the southward, flows through the North Channel, and into the Atlantic. The times of observation were 4 a.m. and 4 p.m., the hours of nearly minimum and maximum temperature, when it was assumed that any differences in the air of night and day, similar to those observed by Lewy over the Atlantic, would be most perceptible. The capacities of the two bottles A and B, which served for all the determinations, were respectively 4815 cb. c. and 4960 cb. c.

The following table, containing all the experiments which were made, gives the results of these determinations:—

TABLE II.

Showing the Amount in Volumes of the Carbonic Acid in 10,000 *Volumes of the Air over the Irish Sea determined by Pettenkofer's Method.*

No.	Date. 1865.	Bar.	Temp. of Air. Dry.	Temp. of Air. Wet.	Temp. of Sea.	Wind, &c.	Carbonic acid. 1st Expt.	Carbonic acid. 2nd Expt.	
1	August 4th	762·5	16·4	11·1	16·0	N.W. by W. Very light	2·66	3·07	Day very fine and clear.
2	,, 5th	762·0	13·9	12·9	15·0	S.W. by S. Light breeze	2·92	3·05	
3	,, 5th	761·2	16·1	14·4	15·0	S.W. by S. ,,	3·08	3·21	
4	,, 7th	753·4	14·2	13·3	15·0	S.W. by S. Light	3·30	3·22	Baryta-water exposed 3 hours.
5	,, 7th	757·5	17·2	15·1	15·6	N.W. ,,	3·20	3·15	Sunny. Very fine.
6	,, 8th	760·2	13·6	12·2	15·0	N.N.W. Moderate	3·06	3·19	
7	,, 8th	761·0	18·3	13·1	16·0	N.N.W. Light breeze	3·32	3·02	Fine and sunny.
8	,, 9th	758·7	13·3	12·2	15·0	S.W. by W. ,,	2·93	3·10	
9	,, 9th	756·4	1[illegible]·0	—	15·0	S. by W. Moderate	3·09	3·23	Rain.
10	,, 10th	749·3	15·0	11·9	14·5	S. by W. Fresh	3·11	3·11	Very wet. Rain all day.
11	,, 12th	750·5	13·4	11·9	14·5	S.W. by W. Strong	3·09	3·10	Windy, and much rain from the 11th to the 16th.
12	,, 16th	752·3	14·7	12·8	15·0	N.W. by W. Light	2·93	2·95	
13	,, 17th	753·1	13·9	12·8	15·0	W.S.W. Fresh	3·12	2·94	Baryta-water exposed 6 hours.

The kindness of Messrs. Alfred Booth & Co., of Liverpool, has enabled me to extend this enquiry to the air of the Atlantic. The following determinations were made in the manner above described during a voyage to and from the Brazils. The four bottles, C, D, E, F, employed in collecting the air, were however of greater capacity, containing respectively 7375 cb. c., 7620 cb. c., 7510 cb. c., and 7560 cb. c. By thus experimenting on a larger volume of air, any variations in the quantity of atmospheric carbonic acid over the sea would of course be rendered more appreciable. On the return passage I was unfortunately unable to make more than one experiment at once, accident having deprived me of all my bottles with the exception of E.

Table III, on the following page, shows the results of these determinations.

The mean quantity of carbonic acid in the atmosphere of the Irish Sea, from 26 experiments, is 3·082; in that of the Atlantic it is, from 51 experiments, 2·953 in 10,000 volumes of air; the mean of the 77 experiments being 3·00.

This result, compared with the following numbers giving the amount of carbonic acid contained in land air, shows that, contrary to the statement of Lewy, the air of the sea contains a much smaller proportion of carbonic acid than that of the land.

The most extensive observations on land-air have given as means:—

Observer.	Locality.	No. of Expts.	Vols in 10,000 of air.
Th. de Saussure	Chambeisy	104	4·15
Boussingault ..	Paris	142	3·97
Verver	Gröningen	90	4·20
Roscoe	London and Manchester	161	3·95
Angus Smith ..	do. do.	200	4·03
General mean of observations on Land-air			4·04
General mean of observations on Sea-air (Lewy, 11 independent experiments)			4·63
General mean of observations on Sea-air (Thorpe, 44 independent experiments)			3·00

The quantity of carbonic acid contained in land-air is subject to continual alteration from the variable circumstances of locality, temperature, fog, rain, &c.; it may thus vary from

TABLE III.

Showing the Amount in Volumes of the Carbonic Acid in 10,000 *vols. of the Air over the Atlantic Ocean, determined by Pettenkofer's Method.*

No.	Date. 1866.	Hour.	Ship's Position. Lat.	Ship's Position. Long.	Bar. mm.	Temp. of Air. Dry.	Temp. of Air. Wet.	Temp. of Sea.	Wind.	Carbonic Acid. 1st Expt.	Carbonic Acid. 2nd Expt.	
			° ′	° ′		°	°	°				
14	Feb. 26th	11.38 p.m.	30·12 N.	16·32 W.	770·0	15·5	13·0	17·7	N.W. by W. Gentle breeze	2·90	2·93	200 miles south of Madeira. Fine.
15	,, 27th	5.24 a.m.	28·43	17·45	761·5	16·2	13·0	17·0	W.N.W. Moderate	2·66	2·83	Off Palma, Canaries. Cloudy.
16	,, 27th	3.50 p.m.	27·47	18·00	758·0	17·6	16·0	19·0	W. by S. Squally	2·83	2·87	Off Ferro, Canaries. Cloudy.
17	,, 28th	3.19 p.m.	26·01	19·09	760·1	18·5	17·5	19·2	do. do.	2·97	2·84	Rain.
18	March 2nd	3.40 p.m.	21·30	23·11	767·1	22·8	17·9	21·7	N. Very light	3·02	3·06	130 miles south of the Tropic. Very fine.
19	,, 3rd	5.15 a.m.	20·15	24·09	766·0	19·6	18·0	—	S. do.	2·97	2·91	Sea calm, and very phosphorescent.
20	,, 3rd	3.0 p.m.	19·17	24·57	765·0	26·0	21·0	22·0	Variable light airs	3·04	3 12	Calm. Baryta-water exposed 5 hours.
21	,, 5th	4.40 a.m.	15·32	27·46	764·5	21·2	21·0	22·0	N.E. Gentle breeze	3·13	3·36	Cloudy. Sea phosphorescent.
22	,, 5th	3.10 p.m.	14·32	28·26	767·2	26·1	23·6	22·5	S.W. Light and variable	2·98	2·94	Fine and clear.
23	,, 5th	do.	do.	do.	do.	do.	do.	do.	do. do.	3·07	2·96	Exposed 3 hours before titration.
24	,, 6th	4.45 a.m.	13·12	29·21	767·1	21·8	21·7	22·5	Variable light breeze	2·83	2·82	Dark; cloudy. Sea phosphorescent.
25	,, 6th	do.	do.	do.	do.	do.	do.	do.	do.	2·96	2·91	Baryta-water exposed 2½ hours.
26	,, 6th	5.10 a.m.	11·59	30·12	764·5	23·5	21·1	23·5	Winds northerly. Gentle	—	—	
27	,, 7th	5.10 a.m.	10·48	31·03	766·5	23·3	20·0	22·5	N.E. by E. Gentle	2·97	2·93	Cloudy. Midway between Africa and America.
28	,, 7th	do.	do.	do.	do.	do.	—	do.	do.	2·99	—	
29	,, 7th	2.35 p.m.	9·50	31·39	766·0	24·2	21·7	24·5	E. do.	2·88	2·90	Cloudy.
30	,, 7th	do.	do.	do.	do.	do.	do.	do.	do.	2·78	2·91	
31	,, 8th	5.35 a.m.	7·34	32·37	766·5	24·2	21·1	24·5	S.E. Fine breeze	2·74	2·89	Daybreak. Sea phosphorescent during former part of night.
32	,, 8th	do.	do.	do.	do.	do.	do.	do.	do.	2·71	2·69	
33	,, 8th	3.15 p.m.	6·48	33·03	760·1	25·6	22·8	25·5	E.N.E. do.	—	—	Cloudy.
34	,, 12th	7.45 p.m.	3·12 S.	38·12	762·5	29·5	26·1	27·2	Light air	3·09	3·01	Calm. 40 miles from Ceara.
35	,, 12th	do.	do.	do.	do.	do.	—	do.	do.	3·02	3·12	
36	,, 13th	3.10 p.m.	3·43	38·34	761·3	28·0	26·0	29·0	N.E. Gentle breeze	3·06	2·98	Off Ceara. Very heavy rain immediately before experiments.
37	July 16th	3.16 p.m.	15·14 N.	26·13	763·5	26·2	22·8	24·5	N. Light breeze	2·94	—	Baryta-water in all following experiments titrated by hydrochloric acid solution.
38	,, 17th	8 0 p.m.	18·21	24·45	764·0	23·9	22·5	23·0	E. by N. do.	—	—	
39	,, 18th	3.0 p.m.	20·09	23·48	764·5	23·6	22·7	23·0	N.E. by E. Moderate	3·05	—	
40	,, 18th	6.40 p.m.	20·28	23·36	765·0	24·3	22·8	22·5	N.E. do.	3·05	—	Cloudy.
41	,, 19th	3.15 p.m.	22·25	22·45	766·4	25·9	22·8	22·5	N.E. by E. Brisk	3·13	—	Fine and clear.
42	,, 19th	9.0 p.m.	22·50	22·28	767·5	24·3	22·5	22·0	N.E. Fresh	3 09	—	
43	,, 20th	11.15 a.m.	23·43	21·37	770·0	26·1	22·8	22·2	N.E. by E. Moderate	2·90	—	Fine.
44	,, 21st	9.0 p.m.	26·19	19·40	770·0	23·4	20·1	21·2	do. do.	3·04	—	180 miles S.W. of Ferro, Canaries.
45	,, 24th	7.30 a.m.	32·26	14·38	770·0	23·3	20·6	22·0	N. Light air	3·00	—	Calm and sunny.
46	,, 25th	10.45 a.m.	33·56	13·05	773·5	23·5	—	21·2	N.E. Gentle breeze	2·97	—	Clear.
47	,, 25th	8.0 p.m.	34·43	12·28	773·5	21·6	20·4	20·5	N.E. Moderate	2·88	—	Midway between Madeira and Lisbon.

2·5 to 8 volumes in 10,000 of air. It would appear, however, from the above experiments that the amount of carbonic acid in sea-air experiences fewer and far less extensive variations; it is sensibly the same in different latitudes, and is constant in the same locality throughout the year. Thus the mean quantity of carbonic acid contained in sea-air between the parallels of 15° and 30° N. latitude was, in the months of February and March, 1866, 2·96 in 10,000 volumes of air, in July of the same year, it was 3·00 volumes. From Saussure and Boussingault's observations a decided difference may be traced between the amounts of carbonic acid in the air of day and night on the land, the air of the night containing more carbonic acid than that of the day, in the proportion of 100 to 92; but from the following table it clearly appears that no such differences are to be discerned in sea-air:

TABLE IV.

Showing Comparative Amounts of Carbonic Acid contained in Sea-Air during Day and Night.

No.	Day.	No.	Night.
1	2·87	2	2·99
3	3·14	4	3·26
5	3·17	6	3·12
7	3·17	8	3·01
9	3·16	11	3·10
10	3·11	13	3 03
12	2·94	15	2·75
14	2·92	19	2 94
16	2·85	21	3·24
17	2 90	24	2·83
18	3·04	25	2·94
20	3·08	27	2·95
22	2·96	28	2·99
23	3·02	31	2·82
29	2·89	32	2·70
30	2·85	34	3·05
36	3·02	35	3·07
37	2·94	43	2 90
39	3·05	45	3·00
40	3·05	46	2·97
41	3·13		
42	3 09		
44	3 04		
47	2·88		

	Day.	Night.
Means	3·011	2·993

The non-accordance of these results with those obtained by Lewy is undoubtedly mainly due to the difference in the methods of analysis employed. Lewy's determinations were made in Regnault's eudiometer, in which, as is well known, the volume of gas is maintained constant throughout the analysis, the relative changes being estimated by the variations in the pressure of that constant volume over or under that of the atmosphere, measured in millimetres of mercury. Thus, as Dr. Frankland has already pointed out (Chem. Soc. Journ. vi, 199), a variation in volume which in the older method of Bunsen, would appear considerable is in that of Regnault only represented by a small numerical expression. This may be clearly illustrated by an actual determination by Lewy of the amount of carbonic acid in the air of Havre, made at Bogota, 2,645 metres above the sea level (loc. cit. p. 190).

	Tube to the Pt wire.	Large tube (open).	Temperature of water in cylinder.	Temperature of barometer.	Barometer.
	m. m.	m. m.			m.
Air dried (moist)	440 00	226 92	15°·65	15°·50	0 ·56090
After absorption of carbonic acid by potash (moist).....	440 ·00	226 90	15°·65	15°·50	0 ·56080

Carbonic acid in 10,000 vols. of air, 3·586.

Let us now suppose that an error of $\frac{1}{20}$ of a millimetre had been made in the first observation, and that thus the corrected pressure appeared to be 334·67 mm. instead of the actual amount 334·58 mm., then the amount of carbonic acid would have risen to 5·996, or a difference would occur in 10,000 volumes of air of 1·51 vol. The greatest difference observed by Lewy between the amounts of carbonic acid contained in the air of day and night over the sea is 2·074 volumes in 10,000 of air. It deserves also to be noted that Lewy's analyses were not made until eighteen or twenty months after the air had been collected; and although Lewy satisfied himself by experiment that air contained in glass tubes for such a length of time experiences no alteration in composition, yet Regnault* has

* Ann. Ch. Phys. [3], xxxvi, 392.

subsequently shown that the exact determination of the amount of atmospheric carbonic acid cannot be made in air thus preserved, since the glass absorbs a portion of the gas.

The main conclusions, therefore, to be drawn from the foregoing experiments are:—

1. That the sea does not act in increasing the amount of atmospheric carbonic acid.

2. But that, on the contrary, the air over the sea contains a much smaller proportion of carbonic acid than the air of the land, although the influence of the sea in abstracting this gas from the atmosphere is not so great as the older experiments of Vogel and Krüger would indicate.

3. That the mean quantity of carbonic acid contained in the normal atmosphere of the ocean is 3·00 in 10,000 vols. of air.

4. That this proportion is constant, or nearly so, in different latitudes.

5. That this proportion is not sensibly influenced by the different seasons of the year.

6. That this proportion does not experience any perceptible diurnal variations.

XVIII.—*On the Amount of Carbonic Acid contained in the Atmosphere of Tropical Brazil during the Rainy Season.*

By T. E. Thorpe.

The following determinations of the amount of carbonic acid contained in the land air of the tropics were made at Pará. This town is the principal port of entrance to the Amazons, and is situated about eighty miles from the sea on the river Grãm-Pará, in lat. 1° 27′ S., and long. 48° 28′ W.; it is built on the verge of a vast primeval forest extending to the sea-coast, and over which the trade winds of the Atlantic regularly blow during the greater part of the year. These determinations were made by Pettenkofer's method in the manner previously described (p. 192). Hydrochloric acid was substituted for oxalic acid in the titration of the baryta-water, since solutions of the latter acid decompose rapidly in the tropics. The following table gives the results of these determinations.

TABLE V.

No.	Date. 1866.	Hour.	Bar. mm.	Temp. of Air.		Wind, &c.	CO_2 in 10,000 vols. of Air.		
				Dry.	Wet.		1st Expt.	2nd Expt.	
1	April 3rd	4.20 p.m.	762·0	23·4	23·1	Light air; overcast	3·19	3·14	After 6 hours' heavy and almost incessant rain.
2	,, 4th	3.0 p.m.	761·4	29·0	27·5	Little wind; gloomy	3·44	3·35	Immediately previous to a storm.
3	,, 16th	11.20 a.m.	766·0	30·1	26·2	N.E. Light breeze	3·47	—	Much rain on previous night; cloudy.
4	,, 16th	3.45 p.m.	763·5	25·6	24·7	N.E. Gentle breeze	3·22	3·13	After 1½ hrs. heavy rain.
5	,, 18th	9.25 a.m.	766·0	27·2	25·0	N.E. Little wind	3·27	3·12	Cloudy; dull.
6	,, 18th	3·5 p.m.	763·5	25·9	25·3	—	3·22	—	After rain.
7	,, 19th	2.30 p.m.	762·5	28·9	25·6	N.E. by E. Fine breeze	3·30	3·12	Sunny.
8	,, 21st	12.50 p.m.	764·0	33·3	26·6	N.E. Gentle breeze	3·41	3·28	Fine.
9	,, 23rd	1.20 p.m.	764·5	28·3	25·9	do. do.	3·12	3·27	Fine and sunny.
10	,, 24th	2.35 p.m.	764·0	32·3	25·6	do.	3·16	3·48	Clear.
11	May 4th	2.50 p.m.	763·3	29·6	26·6	N.N.E. Fine breeze	3·32	—	Fine.
12	,, 7th	3.30 p.m.	762·0	26·9	24·6	Variable and light	3·07	3·14	Gloomy.
13	,, 12th	1.40 p.m.	761·5	27·4	25·6	N.N.E. Fine breeze	3·24	3·35	Gloomy. Immediately before storm of wind and rain.
14	,, 18th	12.15	763·5	30·8	25·6	N.E. Gentle breeze	3·32	3·28	
15	,, 21st	12.45	762·5	29·8	25·6	N.E.	3·31	3·29	Fine and sunny.
16	,, 23rd	11·45	764·5	32·2	27·2	Fine breeze	3·45	3·32	Cloudy.
17	,, 26th	1.0	764·5	31·7	25·0	Fresh breeze	3·49	3·30	Little rain for past three days. Fine.

From the above 31 experiments it appears that the mean quantity of carbonic acid contained in the air of tropical Brazil during the months of April and May, 1866, was 3·28 in 10,000 volumes of air—a very marked difference from the mean proportion (4·0 vols. in 10,000 of air) contained in the atmosphere of Europe, and probably due in great measure to the joint action of tropical rain and tropical vegetation in withdrawing this gas from the air. The influence of rain on the amount of atmospheric carbonic acid is well known from the experiments of Saussure and Bousingault. The annual rainfall at Pará is very heavy, amounting, according to observations kindly furnished to me by Drs. Bruno-Cabral and José Abrea, to nearly three metres (118 inches), of which about one-third falls during the months of March, April, and May. The above determinations are consequently interesting as showing the proportion of carbonic acid in the atmosphere of the tropics in the middle of the rainy season of the year. The amount of carbonic acid contained in the atmosphere of the tropics during the different seasons of the year has already been determined by Lewy*. The mean of an extensive series of analyses of the air of Bogota, in New Granada during the wet and dry seasons of the year is as follows:—

* Loc. cit. p. 190.

	During the rainy season.	During the dry season.
Carbonic acid in 10,000 vols. of air	3·822	4·573

In conclusion, I beg to tender my thanks to Professor Roscoe for the valuable advice and assistance he has given me during these investigations.

XIX.—*On Alloys.*

By A. Matthiessen, F.R.S., Lecturer on Chemistry in St. Mary's Hopital Medical School.

[A Discourse delivered to the Fellows of the Society, February 7th, 1867.]

In the following pages, my object, besides drawing attention to the general nature and properties of alloys, is to show reasons deduced from experiments, for my adoption of certain views on the subject, which may be summed up in a few words, thus:—

I. That, according to certain physical properties, the metals may be divided into two classes:—

Class A. Those metals which impart to their alloys their physical properties in the proportion in which they themselves exist in the alloy.

Class B. Those metals which do not impart to their alloys their physical properties in the proportion in which they themselves exist in the alloy.

The metals belonging to class A are lead, tin, zinc, and cadmium, and those belonging to class B, in all probability, all the rest.

II. That the alloys may be divided into three groups:—

a. Those made of the metals belonging to class A with one another.

b. Those made of the metals belonging to class A with those of class B.

c. Those made of the metals belonging to class B with one another.

III. That in nearly all cases the two-metal alloys may be considered as solidified solutions of the one metal in the other.

Under the term solidified solution I mean a solution of two

substances which has been allowed to solidify, as for instance, if a mixture of ether and alcohol were made, and sufficient cold could be produced to solidify it, we should produce a solidified solution of these two substances in one another. Again, if the chlorides of potassium and sodium, say in equal parts, be melted together and allowed to solidify, the solid thus produced is a solidified solution of the chlorides of potassium and sodium in one another. Glass is also a good example of a solidified solution; to produce it, different silicates are fused together and allowed to solidify. There is, however, an important point in the definition of the term solidified solution which must not be overlooked, namely, that the components are most intimately mixed together; in fact they are homogeneously diffused in one another, and to that extent that, even under the most powerful microscope, it would not be possible to distinguish the components of a solidified solution. As examples of this fact, glass may be quoted, which presents under high magnifying power a homogeneous mass; the silver and gold in the gold-silver alloys cannot be distinguished by the same test from one another.

Such then is a brief outline of what I consider alloys generally to be, and I will now proceed to explain why I have adopted these views; but before entering on the subject, I would state that what I am about to say regards only two-metal alloys made from pure metals. I make this remark, as some of the facts I am about to advance do not agree with those generally accepted.

A most useful piece of apparatus in making alloys for experimental purposes on a small scale is the common clay tobacco pipe, the bowl serving for a crucible, and the stem as a means of passing a gas (hydrogen) through it to mix the melted metals, to prevent oxidation, and afterwards as a form to cast the alloy in, by sucking the contents of the bowl into the stem, by means of an india-rubber tube. This form of apparatus might be made in any size in fire-clay, and would be of great service in experimenting with copper and its alloys.

If to a melted metal, a solid one be added, certain phenomena will be observed which may be classed under the following heads:

I. The solid metal dissolves quickly in the melted one, with evolution of heat, notwithstanding the fact that a cold piece of metal is put into the fused one, and also that a certain amount

of heat is rendered latent by the liquefaction of the solid metal; as examples: gold and just melted tin; sodium and mercury.

II. The solid metal dissolves quickly without evolution of heat; as example: lead and just melted tin.

III. The solid metal dissolves slowly; as example: copper and just melted tin.

IV. Only a partial alloy is formed: or in other words, each metal dissolves to only a limited extent in the other, in the same manner as ether and water, for water will only dissolve a certain amount of ether, and ether a certain amount of water. Now supposing these solutions were well shaken up together and submitted to an intense cold, sufficient to solidify them, the solid mass so produced would not be a solidified solution of ether and water, but a mixture of solidified solutions of ether in water, and water in ether: for no doubt under a high magnifying power the components of the mixture could be distinguished one from the other. Perfectly analogous cases are found with alloys, as examples:

I. Lead and zinc: lead will only dissolve 1·6 per cent. zinc, zinc only 1·2 per cent. lead.

II. Bismuth and zinc: bismuth will only dissolve 8·14 per cent. zinc, and zinc 2·4 per cent. bismuth.

These facts may be easily proved by fusing lead or bismuth in a crucible and adding zinc to the melted metal, when, after the addition of a certain quantity, the zinc alloy being specifically lighter, will float on the surface; or better still, if, say equal parts of the metals be taken, fused, mixed thoroughly, and cast into a mould imbedded in red hot sand and allowed to cool slowly, the separation of the two alloys will be perfect. If on the contrary equal parts of the two metals be fused together, well mixed and cooled suddenly, such an alloy would be analogous to the case of ether and water, a mixture of solidified solution of zinc in lead or bismuth, and of bismuth or lead in zinc.

The physical properties of alloys may be divided into three classes:—

I. Those which in all cases are imparted to the alloy approximately in the ratio in which they are possessed by the component metals.

II. Those which in all cases are not imparted to the alloy in the ratio in which they are possessed by the component metals.

III. Those which in some cases are and in others are not imparted to the alloy in the ratio in which they are possessed by the component metals.

From the last class I shall endeavour to deduce the chemical nature of alloys; it will however be necessary to say a few words regarding the other two classes.

As types of the first class, specific gravity, specific heat, and expansion due to heat, may be taken.

a. Specific Gravity.—With regard to this property it is too well known that the specific gravities of the metals take part in that of their alloys approximately in the ratio of their relative volumes, to need any further comment; but for the sake of illustration I give the following tables, the first containing the values found for the specific gravity of alloys of two metals belonging to class A, and the second those of two metals belonging to class B.

TABLE I.

	Obs. specific gravity.	T.	Cal. specific gravity.
Sn	7·295	12·8	—
Sn_6Pb	7·927	15·2	7·948
Sn_4Pb	8·188	16·0	8·203
Sn_2Pb	8·779	17·2	8·781
Sn Pb	9·460	15·5	9·474
Sn Pb_2.....	10·080	14·8	10·136
Sn Pb_4.....	10·590	14·3	10·645
Sn Pb_6.....	10·815	15·6	10·857
Pb	11·376	13·5	—

TABLE II.

	Obs. specific gravity.	T.	Cal. specific gravity.
Ag	10·468	13·2	—
Ag_6Au	11·760	13·1	11·715
Ag_4Au	12·257	14·7	12·215
Ag_2Au	13·432	14·3	13·383
Ag Au	14·870	13·0	14·847
Ag Au_2	16·354	13·0	16·315
Ag Au_4	17·540	12·3	17·493
Ag Au_6	18·041	13·1	17·998
Au	19·265	12·8	—

(Phil. Trans., 1860, p. 177.)

b. Specific Heat.—In the few cases in which experiments have been made on the specific heat of alloys, it appears that the specific heats of the metals take part in that of their alloys in the ratio of their relative weights, as shown in table III.

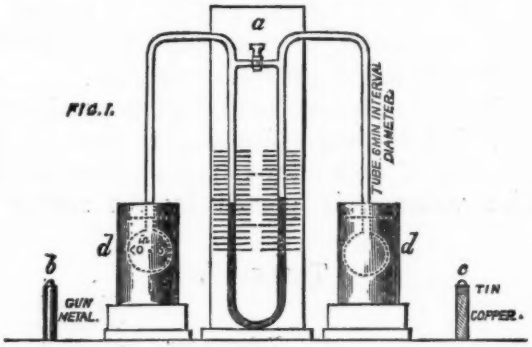
TABLE III.

	Obs. specific heat.	Cal. specific heat.
$PbSn$	0·04073	0·04039
$PbSn_2$	0·04506	0·04461
$PbSb$.....	0·03880	0·03883
$BiSn$.....	0·04000	0·03987
$BiSn_2$	0·04504	0·04415

(Watts' Dict. Chem., iii., p. 33.)

This may easily be shown with the help of an inverted differential thermometer (figure 1), the construction of which

DIFFERENTIAL THERMOMETER.



needs no explanation. The stop-cock *a*, has been found most useful in adjusting the level of the liquid in the bent tube. If an alloy be made (say gun-metal) and cast in a mould, and if, on the other hand, a piece of copper be cast in the same mould and turned down, so that its weight corresponds to the weight of copper in the alloy; and if the amount of tin corresponding to the quantity of tin in the alloy be cast round the top of the copper, two castings will be produced (*b* and *c* figure 1) of equal weights, the one being an alloy, the other its components. These may now be heated in boiling water for a short time and then placed in the cylinders (*d d*), into which equal weights or bulks of water of the same temperature have been poured and

if, after about a minute's immersion, during which time the castings have been kept in motion, the air-thermometer be placed in the water, no difference in the level of the liquid will be observed, indicating that the specific heats of the two castings are the same. On the contrary, if equal weights (about 500 grms.) of two metals having different specific heats be taken, for instance lead and zinc, and if the same process be followed out, a very marked difference will be observed in the indication of the thermometer (about 60 mm. difference in the levels of the liquid in the bent tube). If, however, weights of any two metals be taken, corresponding to their combining numbers, no difference in the heights of the columns will be observed.

This modification of the differential air-thermometer is a simple means of illustrating many experiments on heat, as for instance, latent heat, influence of sources of heat and of salts on the boiling points of liquids, showing that the temperature of steam is not altered by the addition of salt to the water (the practical application of this well known fact is seen in fixing the boiling point of a thermometer), &c.

c. Expansion due to Heat.—That this property also follows the law, namely, that the expansion due to heat of the metals takes part in that of their alloys, approximately in the ratio of their relative volumes, is proved by the results given in table IV.

TABLE IV.

Alloy.	Volumes per cent.	Observed volume at 0° = 1 v. at 100°.	Calculated volume at 0° = 1 v. at 100°.
Sn_4Pb	22·28 Pb	1·007188	1·007225
Pb_4Sn	82·09 Pb	1·008419	1·008129
CdPb	58·49 Pb	1·009138	1·008847
Sn_4Zn	87·46 Sn	1·007184	1·007144
Sn_6Zn	91·28 Sn	1·007058	1·007066
$Bi_{88}Sn$	0·85 Sn	1·004064	1·003972
BiSn	42·81 Sn	1·005098	1·005207
$Bi_{48}Pb$	1·76 Pb	1·004086	1·004026
BiPb	46·26 Pb	1·008621	1·006007
Cu + Zn (71 p. c. Cu)	33·85 Zn	1·005719	1·006328
AuSn	60·85 Sn	1·004233	1·005919
Au_4Sn_7	73·14 Sn	1·004428	1·006223

TABLE IV *(continued)*.

Ag_4Au.....	19·86 Au	1·005166	1·005549
AgAu	49·79 Au	1·004916	1·005123
$AgAu_4$.....	79·86 Au	1·004300	1·004693
Ag + Pt (66·6 p. c. Ag.) ..	19·65 Pt	1·004568	1·005207
Au + Cu (66·6 p. c. Au) ..	48·06 Au	1·004657	1·004716
Ag + Cu (36·1 p. c. Ag) ..	28·31 Ag	1·005436	1·005233
Ag + Cu (71·6 p. c. Ag) ..	73·13 Ag	1·005713	1·005607

A simple mode of showing this is to take a bar of gun-metal and place it as shown (fig. 2.) in a glass tube, fitted at the ends with glass tubes, in such a manner that steam can be blown through it. If now a comparative experiment be made in this manner, first with a bar of gun-metal, and then with a bar made of its components, by soldering together the proper lengths of copper and tin, as shown in the figure, it will be found that the index indicating the expansion, will show in both cases the same readings.

APPARATUS TO SHOW EXPANSION BY HEAT.

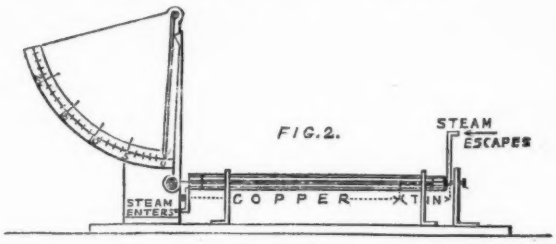


FIG. 2.

II. As types of the second class of physical properties, namely, those which in all cases are not imparted to the alloy in the ratio in which they are possessed by the component metals, the fusing points and crystalline form may be chosen for discussion.

a. Fusing Points.—It has been often stated that the fact of the fusion point of an alloy being lower than the mean fusion points of the component metals, is an indication of chemical combination. But on carefully looking into what is known on the subject, it will be found that all mixtures have a lower fusion point than the mean of the substances forming the mixture. So, for instance, salt water solidifies below zero; chloride of potassium and chloride of sodium fuse at a lower tem-

perature than the mean of the relative volumes of the components, so likewise do mixtures of chloride of potassium with chloride of calcium or strontium, &c. As a practical example of this fact, the fluxes used by metallurgists may be quoted; so also the solder used by various metal-washers; and when decomposing a silicate, we prefer to fuse it with a mixture of the carbonates of potassium and sodium, rather than with either of them alone.

Taking the most simple of these cases, the mixture of the chlorides of potassium and sodium, I may say that nobody has, as yet, asserted in this case, that chemical combination exists between these salts on account of the existence of a lower fusion point than the mean fusing point of the component salts. This property, being a general property of all mixtures (some of the amalgams I believe only excepted), we must arrive at the conclusion, that the fact that alloys fuse more readily than the mean fusing points of the component metals, is by no means an indication of chemical combination.

This fact, I think, admits of explanation as follows:—

It is generally admitted that matter in the solid state exhibits excess of attraction over repulsion, whilst in the liquid state these forces are balanced, and in the gaseous state repulsion predominates over attraction. Let us assume that similar particles of matter attract each other more powerfully than dissimilar ones. It will then follow that the attraction subsisting between the particles of a mixture will be sooner overcome by repulsion than in the case of a homogeneous body: hence mixtures should fuse more readily than their constituents.

b. Crystalline Form.—Various observers have deduced that certain alloys are chemical combinations, owing to their crystallising in definite forms; this has also been often done in the case of carbon-iron alloys; in fact, numerous chemical combinations between these two elements, have been said to be discovered in this manner. It may, however, be asserted, that definite crystalline forms, with alloys, are not necessarily chemical combinations.

Cooke was, I believe, the first to point out this, for he proved that all the alloys of antimony and zinc containing from 43 to 64 per cent. of zinc, crystallise in the same form, but differently from the other alloys of these two metals. With the

gold-tin alloys, it has been shown that well defined crystals are not limited to definite proportions of the two metals, but are common to all alloys of these metals containing from 27 to 43 per cent. gold.

The crystals of these alloys have never the same composition as the mother-liquor from which they were crystallised, but contain always more gold, as is shown by the results contained in table V.

TABLE V.

Composition of alloy.	Amount of gold per cent. in first crop of crystals.	Amount of gold per cent. in	Amount of gold per cent. in mother-liquor.
41·8 Au 58·2 Sn	43·6	2nd crop. 43·6	40·8
40·5 Au 59·5 Sn	42·9	6th crop. 38·7	
37·5 Au 62·5 Sn	39·7	4th crop. 37·6	32·9
35·0 Au 65·0 Sn	37·5	4th crop. 32·6	30·6
32·5 Au 67·5 Sn	36·8	4th crop. 35·2	28·7
30·0 Au 70·0 Sn	33·8	6th crop. 31·5	25·3
25·0 Au 75·0 Su	27·4	....	20·1

Storer has also shown that all the copper-zinc alloys crystallise in the same form, so that crystals of any composition can be obtained.

In considering this property, we must bear in mind the influence of traces of foreign matter on the crystallisation of all substances. Thus many pure metals may be made to crystallise more readily, if a trace of another metal be added; for instance, antimony to which a trace of tin is added

crystallises much more readily, and in much larger crystals than the pure metal. With lead the case is reversed, for in this case, the purer the lead the larger the crystals. With salts we find analogous behaviour; so, for instance, chloride of ammonium when dissolved in pure water crystallises in small crystals, but when a small quantity of tarry matter is added to the solution, it crystallises readily in large cubes; common salt crystallises from water, as is well known, in cubes; from urine, or from water containing urea, in octohedrons.

The fact that two metals are capable of alloying with each other and producing definite crystalline forms, in other proportions than those of their combining weights, ought always to be borne in mind, when discussing the chemical nature of a metallic compound.

III. As types of the third class of physical properties, namely of those which in some cases are, and in others are not, imparted to the alloy in the ratio in which they are possessed by the component metals, the conducting power for heat and electricity, sound, elasticity, and tenacity, may be taken.

a. Conducting Power for Electricity.—The values obtained for the conducting powers of alloys prove that this property belongs to this class.

Table VI contains the values employed in calculation.

TABLE VI.

Metal. All hard-drawn.	Atomic weight.	Specific gravity.	Specific conducting power of metre length and millimetre diameter, in terms of the BA unit.
Silver	108	10·5	47·5
Copper....	63·5	8·9	47·5
Gold.....	197	19·3	37·1
Zinc	65	7·1	13·8
Cadmium..	112	8·6	11·3
Tin	116	7·3	5·9
Lead.....	207	11·4	4·0
Iron	—	—	8·0

Tables 7, 8, and 9 contain a few examples of each group of alloys. Table 7, those of class A with one another. Table 8, those of class A with class B. Table 9, those of class B with one another.

TABLE VII.

Alloy.	Volumes per cent.	Specific conducting power of metre length and millimetre diameter, in terms of the BA unit. Observed.	Calculated.
Sn_4Pb	83·9 tin	5·7	5·6
Sn_4Cd	83·1 „	6·9	6·8
Sn_2Zn	77·7 „	7·9	7·6
PbSn	53·4 lead	4·8	4·9
$ZnCd_2$	26·1 zinc	12·2	12·0
$SnCd_4$	23·5 tin	10·3	10·0
$CdPb_6$	10·6 cadmium	4·3	4·7

TABLE VIII.

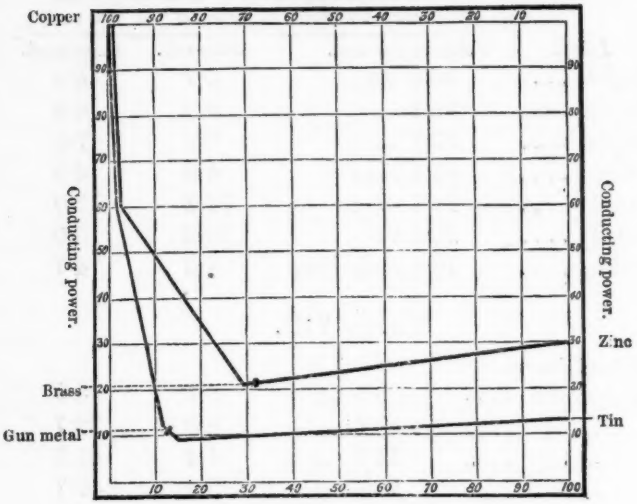
All hard-drawn.			
Copper-tin	93·6 tin	5·7	8·5
„	83·6 „	6·0	12·7
„	14·9 „	4·2	41·3
„	11·6 „	5·9	42·7
„	6·0 „	9·4	45·0
„	1·4 „	29·7	46·9
Copper-zinc	42·1 zinc	10·4	33·3
„	29·4 „	10·3	37·6
„	23·6 „	13·4	39·6
„	10·9 „	22·1	43·9
„	5·0 „	28·7	45·8

TABLE IX.

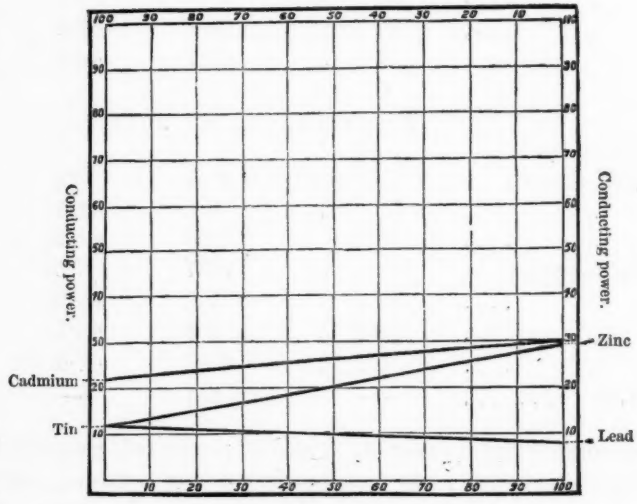
All hard-drawn.			
Gold-silver ..	79·9 gold	10·1	39·2
„	52·1 „	7·1	42·1
„	19·9 „	10·3	45·4
Gold-copper	98·4 „	26·7	37·3
„	81·7 „	7·6	39·0
„	19·2 „	9·8	45·5
„	0·7 „	40·0	47·4
Steel	—	6·3	—

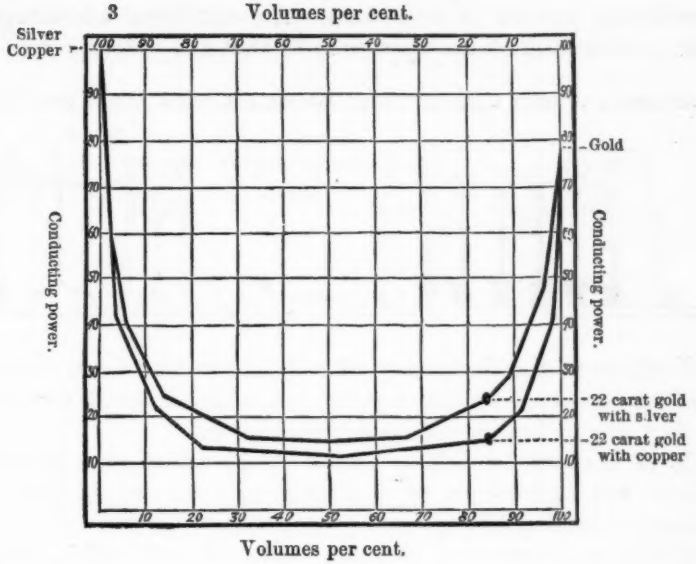
The accompanying curves, 1, 2, and 3, represent graphically the values obtained for the conducting powers of some alloys of each group, the conducting power of silver being taken, for convenience sake, to equal 100.

1 Volumes per cent.



2 Volumes per cent.



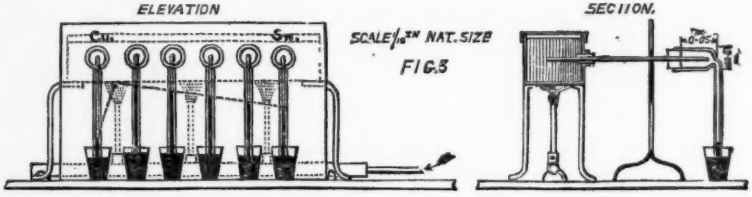


From these it will be seen at a glance that the alloys belonging to metals of the class A conduct electricity in the ratio of the relative volumes of the component metals, whilst the others do not. It will be as well to draw attention at once to the marked change which takes place in this property, when a metal belonging to class B is alloyed, either with one of its own class, or with one belonging to class A; and also to the fact, that when a metal belonging to class A is alloyed with one of class B., no such change takes place. This behaviour is observed with all the physical properties belonging to this class.

b. Conducting Power for Heat. — Wiedemann and Franz have shown experimentally, that the conducting powers for heat and electricity for metals and alloys are identical. The conducting power for heat may be conveniently shown with the help of the apparatus represented in fig. 3. If bars of copper, copper-tin alloys of various compositions, and tin be made and fitted in the box, as shown in the figure, with small air-thermometers at their ends, and boiling water be poured into the box (which may be kept boiling with lamps underneath), the depressions in the columns of liquid in the air-

thermometers will approximately show the ratio between the conducting powers of these bars. An additional advantage of this modification of the apparatus is that the differences of the

APPARATUS TO SHEW CONDUCTIVITY OF METALS AND THEIR ALLOYS FOR HEAT.



indications of the thermometers remain constant for some time. The curve formed by the tops of the columns would represent, in fact, the resistance-curves for electricity.

It is obvious, by taking series of the other two groups of alloys, the indications of the thermometers would give the resistance-curves corresponding to those alloys.

This method gives us, therefore, a simple and striking means of showing the sudden or gradual alteration in conductibility in the three groups of alloys.

It is scarcely necessary to mention that screens must be placed between the box and the air-thermometers, to prevent the thermometers being heated by radiation.

c. Sound.—If bars of copper, tin, zinc, or lead, suspended by a string, be struck, they all emit a dead sound; if, on the contrary, bars of copper-tin (gun-metal) or copper-zinc (brass) be struck, they will emit a clear ringing note, showing the marked effect of alloying a metal of class B with one of class A. Conversely, if we strike bars of tin-copper (containing 12 p. c. copper), or tin-lead (containing 20 p. c. lead), they will emit a dead sound, showing, as in the cases of conduction of heat and electricity, no marked change when metals of class A are alloyed with one another, or with one belonging to class B. The same effects will be produced when bars of wrought iron and steel are struck, the first emitting only a slight sound, the second a clear ringing note.

d. Elasticity.—When a weight is hung to spirals of hard drawn wires of the same diameter, both in wire and coil, different effects will be produced (diameter of wire No. 23 wire-gauge, diameter of coil about 7 mm. weight used 500 grms.)

The copper, silver, gold, and platinum spirals will be almost lengthened to a straight wire.

The tin, zinc, copper-tin (12 p. c. copper) and tin-lead spirals will be almost lengthened to straight wires, with only 50 grms.

The copper-tin (gun-metal), brass, platinum-silver (33 p. c. platinum), and gold-copper (22 carat) spirals will be only lengthened to a small extent with 500 grms.

The iron spiral may be made to lengthen with 500 grms. weight, especially on shaking the spiral; but that of steel does not lengthen at all under the same conditions.

Here then, again, we see the marked change in this property, when a class B metal is alloyed with one of its own class or with one of class A, as well as the absence of any marked change when a class A metal is alloyed either with one of its own class, or with one of class B.

e. Tenacity.—With the help of a draw-bench and spring-balance, wires may be broken, to show in a rough way their relative tenacity. The values in the following table must be considered as only approximative, but they will nevertheless show the fact, that as soon as a metal belonging to class B is alloyed with another, its tenacity is greatly increased.

All hard-drawn wires, gauge No. 23; for convenience sake double wires were used in the experiments.

TABLE X.

	Breaking strain for double wire.
Copper	25—30 lbs.
Tin	under 7 „
Copper-tin (12 p. c. tin)	80—90 „
Tin-copper (12 p. c. copper)	about 7 „
Lead	under 7 „
Tin-lead	„ 7 „
Gold	20—25 lbs.
Gold-copper	70—75 „
Silver	45—50 „
Platinum	45—50 „
Silver-platinum	75—80 „
Iron	80—90 „
Steel	above 200 lbs.

The foregoing experiments tend to prove that the physical

properties belonging to this class follow the law; that as soon as a metal belonging to class B is alloyed with one of class A, or with one of its own class, a very marked change in the physical properties takes place, they no longer being equal to the mean of the relative weights or volumes of the component metals. That the curves representing their numerical values, would have analogous forms, is proved, not only by the foregoing data, but also by the fact that the turning points of the electric conducting power curves represent approximately the composition of technically used alloys, such alloys being used on account of some special physical property.

Thus, gun-metal (10 p. c. tin) is marked on the copper-tin curve, its turning point corresponding to 12·5 p. c. tin.

Brass containing 28 p. c. zinc is marked on the copper-zinc curve, the turning point of which corresponds to 25 p. c. zinc.

22 carat gold alloyed with silver is marked on the silver-gold curve, and the same alloyed with copper on the copper-gold curve.

When the Electrical Standard Committee appointed by the British Association arranged their unit-coil, they chose the alloy containing 33 p. c. platinum, on account of its being the turning point of the silver-platinum curve, and from its possessing certain electrical properties which rendered it eminently fit for the purpose. It was afterwards found that this alloy had been in use for many years on account of its high elasticity as a dental alloy.

The question now arises what are the alloys at the turning points of these curves? Are they chemical combinations, or are they not, and if not, what are they?

If they are chemical combinations, then we should have to accept the following formulæ:—

The alloy composed of 87·5 copper and 12·5 tin would correspond to about.....	$Cu_{13}Sn$
The alloy composed of 75 copper and 25 zinc to	Cu_3Zn
The alloy composed of 22 gold and 2 silver to ..	Au_6Ag
The alloy composed of 22·1 gold and 2 copper to	$Au_{17}Cu_2$
The alloy composed of 66·6 silver and 33·3 platinum to	$Ag_{17}Pt_2$
The alloy composed of 99·3 bismuth and 0·7 tin to	$Bi_{88}Sn$
The alloy composed of 98·0 bismuth and 2·0 lead to	$Bi_{48}Pb$

The above alloys represent the turning points of the electric conducting power curves expressed in weights. Now it has just been pointed out that the curves which would numerically represent the third group of physical properties would have analogous, but not identically the same form: hence it follows that the turning points of these curves may vary several per cent. in their composition. Are then these also chemical combinations? I think however that the idea of the existence of chemical combinations at these points must be given up, owing to such abnormal combinations as the above, which must then exist, and also owing to the immense number of them having nearly the same composition as the curves representing each of the physical properties of the third group, having in all probability slightly different turning points; and if in the one case they be chemical combinations, why should they not be in the other?

The great similarity in the forms of the curves representing the electric conducting powers of alloys speaks also against the turning points being chemical combinations:—for with the first group of alloys they are nearly straight lines; with the second there is a rapid decrement on the side beginning with the metal belonging to class B; and then it turns and goes in a straight line to the metal belonging to class A. The letter L would represent the typical form of these curves; and with the third there is a rapid decrement on both sides of the curve, the turning points being connected with each other by nearly straight lines; the letter U would represent the typical form of this class of curves.

Having thus shown the probability of the non-existence of chemical combinations at these points, the next step is to indicate the probable cause of the marked changes in the physical properties of a class B metal when entering into an alloy. The experiments detailed tend to show that the third group of physical properties of the metal belonging to class B, when it enters into an alloy with one of its own class or with one of class A, undergo a change, and this change is brought about by a small quantity of the other metal, the quantity of metal required for the completion of this change being dependent on the metal employed; in other words, the class B metal enters into an alloy in an allotropic condition, which modification possesses other physical properties than the original metal:

further, when a metal belonging to class A enters into an alloy, it retains in the alloy its original physical properties.

If the turning points of the curves be now examined from the above point of view, the following facts may be deduced. Taking the copper-tin, copper-zinc, bismuth-tin, and bismuth-lead turning points as examples, table 11 contains the numerical data for these alloys.

TABLE XI.

Composition of Alloy.				Conducting power of alloy in terms of the B.A. unit for metre length and millimetre diameter.
Copper	·851	Tin	·149	4·19
„	·706	Zinc ..	·294	10·33
Bismuth ..	·9905	Tin	·0885	0·117
„ ..	·982	Lead ..	·018	0·122

From the above hypothesis the metals, lead, tin, and zinc enter into alloys with their normal physical properties: hence the part these metals take in the conducting power of the above alloys may be calculated, and will be found, for tin in the first alloy, to be equal to 0·88 for 5·88 × ·149 = 0·88.

For zinc in the second alloy, it will be found equal to 4·0(
For tin in the third alloy, it will be found equal to.. ·05(
For lead in the fourth alloy, it will be found equal to ·071

the conducting powers of these metals being in terms of the B.A. unit, equal to tin 5·88, lead 3·96, and zinc 13·80.

With the first alloy the conducting power for allotropic copper may be found by subtracting the value found for the tin in the alloy from the conducting power of the alloy itself, the value then for the ·851 of copper will be found.

Thus, 4·19 − 0·88 = 3·31, this last value representing ·851 allotropic copper; or a wire of a metre length and millimetre diameter of allotropic copper will have a conducting power equal to 3·89.

From the copper-zinc alloy the value of ·706 copper will be found equal to 6·27; or 1 metre, &c., copper has a conducting power equal to 8·89.

From the bismuth-tin alloy the value of ·990 bismuth will be found equal to 0·0670; or 1 metre, &c., bismuth has a conducting power equal to 0·0677.

From the bismuth-lead alloy the value of ·982 bismuth will be found equal to 0·050; or 1 metre, &c., bismuth has a conducting power equal to 0·0520.

The conducting power of the allotropic copper when alloyed with tin is found to be 3·89, and when with zinc 8·89.

Now, at first sight there seems no connection between these numbers, but when they are divided by the conducting powers of tin and lead respectively, the quotient will be nearly the same:—

$$\frac{3{\cdot}89}{5{\cdot}88} = 0{\cdot}662, \text{ and } \frac{8{\cdot}89}{13{\cdot}8} = 0{\cdot}644.$$

If the values deduced for the conducting powers of bismuth be divided in like manner by those of tin and lead, the same result will be obtained, thus:—

$$\frac{0{\cdot}0677}{5{\cdot}88} = 0{\cdot}00115, \text{ and } \frac{0{\cdot}0520}{3{\cdot}96} = 0{\cdot}00130.$$

These values agree together as well as can be expected, considering that the turning points have not been absolutely determined, and that a small percentage difference will account for the differences between them.

It may, therefore, be supposed, although it has been only proved in these two cases, that when copper or bismuth enters into an alloy, their conducting powers alter as follows:—

The conducting power of copper will be = 0·65 × the c. p. of the metal alloying it; and that of bismuth = 0·00123 × the c. p. of the metal alloying it.

What the above empirical deduction means I am at a loss, at present, to understand, but the data I am at present acquiring will no doubt throw some light on the subject.

From the above point of view, most of the alloys made of metals of class A, with one another, may be regarded as:—

Solidified solutions of the one metal in the other.

Those made of class A with those of class B (say equal parts) as—

Solidified solutions of the allotropic condition of the class B metal and the class A metal in one another.

And those of class B (say equal parts) with one another as—

Solidified solutions of the allotropic conditions of the one metal in that of the other.

In the description of the foregoing experiments in connection with the third class of physical properties, it will be seen that

I have always made a comparison between iron and steel. This has been done to show that the carbon-iron alloys behave in an analogous manner to other alloys, which cannot be looked upon as chemical combinations. Now, although many are of opinion that because the carbon in some sorts of cast-iron can, under certain conditions, be evolved as carburetted hydrogen, there exists between these two elements chemical combinations, it is more than probable, that the carbon, when in the fine state of division in which it must exist in such specimens, if they be solidified solutions, may possess properties which do not belong to it in its denser form. It seems almost inconceivable that chemical combination between two elements should simply be dependent on the various rates of cooling, for it is possible to produce, with some specimens, so-called chemical combination of carbon and iron (white iron), or the mechanical mixture of carbon and iron (grey iron), merely by cooling the molten mass quickly or slowly. The analogy of cast-iron and steel with other alloys, indicates the non-existence of chemical combinations between carbon and iron.*

There seems to be but little doubt that between certain metals there may exist chemical combinations, as between gold and lead, or zinc, or tin; and in the cases of some of the amalgams, the existence of chemical combinations is indicated:

1. By the fact that a large amount of heat is set free when they are alloyed with one another.

2. By the fact that the alloys do not possess the typical properties of the groups to which they belong.

At present so little is known with regard to the chemical, as well as the physical behaviour of these alloys, that until they have been better studied, it is unnecessary to enter more fully into the subject.

Before concluding I cannot but thank Mr. Bassett for his valuable assistance in carrying out and arranging the above detailed experiments, especially those with the differential air-thermometer, as well as those with the method for showing conduction for heat; to him is due, as much as to myself, any credit in employing the modifications described, as we worked them out and arranged them conjointly.

* See Reports on the Chemical Nature of Alloys and of Cast-iron (Brit. Assoc. Rep. 1863 and 1866).

XX.—*Note on some Varieties of Orchella Weed, and products obtained from them.*

By John Stenhouse, LL.D., F.R.S., &c.

In 1848* I examined two varieties of *Rochella tinctoria*, one obtained from the Cape of Good Hope, and the other, as I was then informed, from the neighbourhood both of Lima and of Valparaiso. Both of these lichens were much larger than the *Rochella tinctoria* produced by the Cape de Verd Islands. "*The South American lichen was from six to eight inches long, and its stems in some instances as thick as those of a goose quill.*" Both of these lichens were pronounced by the eminent botanist Dr. Scouler, of Glasgow, to be large varieties of the *Rochella tinctoria*. I have recently submitted specimens of these lichens to Mr. Bennet, of the Botanical Department of the British Museum, and his assistant, Mr. Carruthers, by whom Dr. Scouler's opinion was confirmed. On showing the South American variety to Messrs. Benjamin Smith and Son, the oldest and most extensive manufacturers of archil in London, they at once recognized it as *Rochella tinctoria*, from Chili, known in commerce as Valparaiso weed, which is but rarely imported into this country; while the so-called Lima weed, which is largely imported, is *Rochella fuciformis*, like that of Angola, Zanzibar, Madagascar, &c.

The colour-yielding principles which I extracted from the Valparaiso and Cape of Good Hope weeds I described under the name of α and β orsellic acids. From the results of my analyses, and from their reactions, which agreed precisely with those of lecanoric acid, Gerhardt inferred that both my α and β orsellic acids were identical with the lecanoric acid of Schunck, and consequently that the acid produced by acting on them with baryta or lime was orsellinic acid. I have since made experiments which convince me that Gerhardt's conjectures are perfectly correct. In the Ann. Ch. Pharm., cxxxix, 22, Hesse gives the analysis of *Rochella tinctoria* (De Cand.) from the Cape de Verd Islands, which, as might be expected, he finds to yield lecanoric acid; and also of the *Rochella fuciformis* (Achar.) from

* Phil. Trans., 1848, p. 63. Ann. Ch. Pharm, lxviii, 55.

Angola, Zanzibar, Madagascar, Ceylon, and Lima, all of which he finds yield erythrin (*erythric acid*). What is now known in commerce as Lima weed is *Rochella fuciformis*, and, therefore, entirely different from the archil weed (*Rochella tinctoria*) analysed by me in 1848, which I then described as from the "*neighbourhood both of Lima and Valparaiso.*" This explains the apparent discrepancy between my results and those of M. Hesse, his Lima weed being *Rochella fuciformis*, whilst mine was the *Rochella tinctoria*, now known in commerce as Valparaiso weed. It is very difficult to ascertain the exact locality from which these lichens are obtained, as importers, for obvious commercial reasons, are very averse to give information on the subject.

On the Preparation of Orcin and Erythrite.

For the extraction of erythrin from *Rochella fuciformis*, I followed the process first described by me in 1848, with the following slight modifications:—3 lbs. of the lichen are macerated for 20 minutes with a milk of lime made by slaking ½ lb. of lime in 3 gallons of water, and the partially exhausted weed is then treated with a fresh quantity of milk of lime. A third maceration is found completely to exhaust the lichen. These weak lime-liquors are employed instead of milk of lime in extracting fresh quantities of weed, whilst the first and strongest liquor is filtered as rapidly as possible through bag filters about 6 inches wide and 6 feet long, which will be found the most convenient for this purpose; and the clear liquor, as it comes through, is immediately precipitated by hydrochloric acid, as protracted contact with the lime decomposes a portion of the erythrin. The precipitated erythrin is collected in bag filters, and when the greater portion of the mother-liquors have thus been removed, it is freed from adhering hydrochloric acid and chloride of calcium by being washed once or twice. This is best accomplished by stirring up the erythrin with a considerable quantity of water, and again collecting it. To transform the erythrin thus obtained into orcin and erythrite, it is again dissolved in a slight excess of milk of lime, and boiled for half an hour in a vessel furnished with a long condensing tube, so as to exclude the air which, as observed by De Luynes, prevents, in a great measure, the formation of a deep red-coloured

resinous matter. The solution, now containing orcin and erythrite, is filtered, the excess of lime removed by passing a stream of carbonic acid gas through it (or more conveniently, on a large scale, by exactly neutralizing with dilute sulphuric acid), and evaporated nearly to dryness, first over a sand-bath, and finally over a water-bath. As orcin is tolerably soluble in benzol, whilst erythrite and the dark-brown colouring matter are insoluble in that menstruum, their separation is best effected by treating the mixture above described with benzol boiling between 110°—150° (toluol, &c.) in a flask of tin, or any other metal, connected with a condenser and heated in a paraffin bath. As the distillation proceeds, the water contained in the mixture of orcin and erythrite distils over with a portion of the benzol. After 20—30 minutes' digestion, the flask is disconnected from the condensing apparatus, and the nearly colourless solution of orcin in benzol is poured out of it, and agitated in a glass flask with about one-tenth of its bulk of water. This extracts the orcin from the benzol, which, after separation, may now be poured back into the tin flask, and the digestion continued as before. After this operation has been repeated three or four times, the solid matter in the tin vessel is extracted by boiling water, filtered when cold to separate resinous matters and other impurities, and evaporated nearly to dryness. After standing several days, a large quantity of erythrite crystallises out. This may be purified by washing with cold spirit, pressing, and recrystallising once or twice from hot water. The aqueous solutions of orcin obtained by the above method, on cooling, usually deposit a quantity of nearly colourless crystals, and the whole of the orcin is readily obtained by sufficient concentration. When it is wished to obtain colourless orcin, we have only to purify by a second treatment with benzol, and recrystallisation from water. The advantage of the above described method consists in enabling us not only easily to separate orcin and erythrite, but also to obtain pure orcin with comparative facility from mixtures contaminated with large quantities of colouring matter.

Action of Chloride of Sulphur on Orcin.

When orcin in fine powder is added to subchloride of sulphur, hydrochloric acid is evolved, and a large quantity of a sulphur-

yellow compound is produced, which is amorphous, and insoluble in water, alcohol, ether, benzol, bisulphide of carbon, and chloroform. It is soluble in caustic alkalis, with partial decomposition, and when strongly heated it is decomposed, but does not sublime.

Orsellinic Ether.

The pasty erythrin, as extracted from the "orchella weed," after being dried at a very gentle heat, is digested for five hours with eight times its weight of alcohol (anhydrous is the best), the greater portion of the alcohol distilled off, and the residue evaporated nearly to dryness on a water-bath. The viscous substance thus obtained is boiled with 10 parts of water, allowed to cool, collected, pressed, and dried at 100°. This mixture of orsellinic ether, picroerythrin, and resinous matter, is boiled with 20 times its weight of benzol for half an hour, and by this means the ethylic orsellinate, being very soluble in hot benzol, is perfectly separated from the picroerythrin and other impurities, which are quite insoluble in that menstruum. On distilling off the benzol, the ether is obtained in comparatively large crystals, which, after one or two crystallisations from hot water, are perfectly pure. This method has great advantages over the ordinary one of repeated crystallisations from water, as the crude ether contains a resinous substance which greatly impedes filtration; and picroerythrin being soluble in water, can only be separated from the ether by this means with great difficulty. In fact, I have found that orsellinic ether prepared by the old method, after three crystallisations from water, leaves a residue of picroerythrin on being dissolved in benzol. This will account for my statement in the Proceedings of the Royal Society, xii, 263, that orsellinic ether, on being boiled with lime, yields small quantities of erythrite.

Diiodorsellinate of Ethyl.

This substitution-compound is obtained by acting on ethylic orsellinate with chloride of iodine. For this purpose a cold saturated aqueous solution of the ether is precipitated by a dilute solution of chloride of iodine containing excess of iodine. Great care must be taken to use a very dilute solution of chloride of iodine, and not to precipitate the whole of the ether.

The white precipitate is collected, washed well with cold water, in which it is almost insoluble, dried, and dissolved in about 10 times its weight of hot bisulphide of carbon. After filtration to separate impurities, a portion of the bisulphide is removed by distillation, and the solution allowed to cool. The crystals of ethylic diiodorsellinate thus obtained are purified by several recrystallisations, first out of bisulphide of carbon, and finally out of spirit. It crystallises from its solutions in small needles. It is moderately soluble in benzol, bisulphide of carbon, and boiling alcohol; much less so in cold spirit, and but very slightly soluble in boiling water, from which it separates in the crystalline state on cooling. It can be heated to 100° without decomposition; at a higher temperature it melts, and on increasing the heat, decomposes, giving off vapours of iodine. Its alcoholic solution decomposes after some time. The following are the results of its analysis:—

I. ·320 grm. gave ·333 grm. AgI.
II. ·314 grm. gave ·328 grm. AgI.
III. ·331 grm. gave ·325 grm. CO_2, and ·072 grm. H_2O.

		Per cent.	I.	II.	III.
C_{10}	= 120	26·79	—	—	26·79
H_{10}	= 10	2·23	—	—	2·41
I_2	= 254	56·69	56·23	56·45	—
O_4	= 64	14·29	—	—	—
	448	100·00			

The formula is $C_{10}H_{10}I_2O_4 = C_8H_5I_2(C_2H_5)O_4$.

Orsellinate of Methyl.

This was prepared by the same process as the ethyl compound, substituting methylic for ethylic alcohol.

Diiodorsellinate of Methyl.

This compound was prepared and purified in the same manner as the corresponding ethyl-compound. Like that substance, it crystallises in needles, and is soluble in benzol, bisulphide of carbon, spirit, and boiling water. It is not decomposed at 100°, but at a higher temperature melts, and gives off iodine.

The iodine determination corresponds to the formula

$$C_9H_8I_2O_4 = C_8H_5I_2(CH_3),O_4.$$

·353 grm. gave ·381 grm. AgI.

		Per cent.	I.
C_9	= 108	24·89	—
H_8	= 8	1·84	—
I_2	= 254	58·52	58·32
O_4	= 64	14·75	—
	434	100·00	

Mode of Estimating the amount of Colour-yielding Matter in Lichens.

In my first paper on lichens in the Philosophical Transactions for 1848, already referred to, I gave two methods for determining the amount of colour-yielding principles in lichens. One of these consisted in exhausting the lichen with milk of lime, precipitating with acetic acid, collecting the precipitate on a weighed filter, drying it at the ordinary temperature, and then weighing it. In this way the amount of colouring principle was directly determined. The only objection to this method is that it is tedious and difficult for any but a chemist to perform. The other consisted in the employment of a standard solution of hypochlorite of calcium. For this purpose "any convenient quantity of the lichen, say 100 grains, is cut into very small pieces, and then macerated with milk of lime till all the colouring principle is extracted. Three or four macerations are quite sufficient for this purpose, if the lichen has been sufficiently comminuted. The clear liquors should be filtered and mixed together. A solution of bleaching powder of known strength should be added to the lime-solution from a graduated alkalimeter. The moment the bleaching liquor comes in contact with the lime-solution of the lichen, a blood-red colour is produced, which disappears in a minute or two, and the liquid has only a deep-yellow colour. A new quantity of the bleaching liquid should then be poured into the lime-solution, and the mixture carefully stirred. The operation should be repeated as long as the addition of the hypochlorite of calcium causes the production of the red colour, for this shows that the lime-solution still contains unoxidized colouring principle. Towards the end of the pro-

cess the bleaching solution should be added by only a few drops at a time, the mixture being carefully stirred between each addition. We have only to note how many measures of the bleaching liquor have been required to destroy the colouring matter in the solution, to determine the amount of the colouring principle it contained."

Improved Process.—100 grains of the lichen are macerated with a dilute solution of caustic soda, two treatments being sufficient to extract the whole of the colouring matter. The amount of colour-yielding principle in this solution is then determined, as in the above process, employing a solution of hypochlorite of sodium, instead of the corresponding calcium-salt. The great advantage is that the liquor remains perfectly transparent, no turbidity being produced, as in the preceding process, by precipitation of carbonate of calcium.

XXI.—*Limited Oxidation: Determination of the Oxygen Consumed.*

By Ernest Theophron Chapman.

It has been shown on a former occasion that when the acids of the acetic series are once produced by the action of dilute chromic acid on organic substances, these acids withstand all further oxidation by the re-agent which has produced them. It has further been shown that so rigidly is this true, that an accurate determination of the carbon in certain organic substances may be made by weighing the organic acids produced in the form of baryta-salts.

In fact, the oxidation down to the fatty acids takes place with almost mathematical precision. This is brought out very strikingly by the close agreement between the "oxygen consumed," as given by actual experiment, and as given by calculation. Some idea of the severity of the test afforded by a determination of the "oxygen consumed" may be derived from the following examples:—

Butyric ether furnishes on oxidation butyric and acetic acids, and nothing else. Now, if five per cent. of the butyric acid (not five per cent. of the mixed acids, but of the butyric

acid only) were to undergo the minimum oxidation, of which, in the presence of chromic acid, it is theoretically capable, viz., conversion into propionic and carbonic acids, and water, we should find that for every hundred parts of oxygen theoretically requisite to convert the ether into acetic and butyric acids, 103·77 would be required. Had the ether contained five per cent. of butyrate of methyl, 103·6, instead of 100, parts of oxygen would be required. Had it contained five per cent. of alcohol, 107·6, instead of 100 of oxygen, would be required.

Neither of the foregoing instances of impure ethers could be detected by a combustion, nor would a combustion show any perceptible difference had the ether contained five per cent. of butyric acid. Had the ether contained five per cent. of butyric acid, of water, or of any non-oxidizable substance, the amount of oxygen consumed would, of course, fall five per cent.; and, indeed, would fall directly with the percentage of impurity. From these examples it is obvious that the great advantage of this method, as well as the chief difficulty in the way of its general employment, is its extreme delicacy; and, indeed, I experienced the greatest difficulty in obtaining substances in a sufficient state of purity wherewith to prove the method.

The determination of the oxygen consumed may be made by determining the amount of sesquioxide of chromium resulting from the reduction of the chromic acid. There are two objections to this mode of procedure.

First. Since chromic acid is present, it is necessary to precipitate the sesquioxide of chromium with potash or soda; not with ammonia. The washing out of the potash or soda-salt is a practical difficulty.

Secondly. There is a degree of uncertainty about the equivalent of chromium which is fatal to its employment in all cases in which great accuracy is required.*

For these reasons I prefer to determine the chromic acid remaining in the liquid after the digestion, and subtract this from the known quantity employed. This estimation I make by means of oxalic acid. In the first instance, I determine the strength of the chromic solution by treating a weighed portion of it with excess of oxalic and sulphuric acids. The carbonic acid liberated I absorb and weigh. To determine the

* Watts's Dictionary, vol. i, page 946; excluding the old determination of Berzelius, the numbers given range from 25·99 to 26·78, a difference of 2·95 per cent.

amount of oxygen consumed by any organic substance, I take a weighed quantity of the substance, and digest it with a weighed excess of the chromic solution. I then in the same manner determine the amount of chromic acid remaining unreduced. The difference between the two amounts of carbonic acid liberated indicates the amount of oxygen consumed. The apparatus employed is simple. A flask with a tube let into its neck is the generating flask; its mouth is closed with a cork, through which passes a stop-cock tube. The tube from the neck of this flask is connected with the top of a bulb pipette, the other end of which passes to the bottom of a small two-necked Woulfe's bottle, containing not quite enough sulphuric acid to fill the bulb of the pipette. This apparatus serves to dry the gas, which is, however, further dried by passing it through a U-tube containing pumice-stone moistened with sulphuric acid. The absorption apparatus, which is in communication with the U-tube, consists of a pipette and Woulfe's bottle, like the drying apparatus, containing caustic potash. The second neck of this Woulfe's bottle communicates with a Liebig's potash apparatus, the other end of which opens into a small drying tube, containing lumps of caustic potash. The whole absorption apparatus, when charged, weighs about 190 grammes. To use the apparatus, the absorption apparatus is detached and weighed, having previously been allowed to stand for some time in cold water, and to hang for half an hour in the balance case. It is then, of course, replaced. The chromic solution is then poured into the generating flask, which should already contain some broken up tobacco-pipe.* The chromic solution must be cold. The oxalic acid solution, together with some dilute sulphuric acid, both cold, are now added by means of an ordinary funnel. This may be done with perfect safety, as no carbonic acid is evolved for some minutes after the mixture is made. The mouth of the flask is then closed with the cork and stop-cock tube. In a few minutes the evolution of carbonic acid commences, and the air is expelled in large bubbles through the apparatus. Of course the apparatus con-

* This substance was recommended to me by Mr. Duppa. Its advantages over everything that I have ever seen in use for preventing bumping induces me to mention it here. When the chromic acid solution contains traces of high acids, it bumps tremendously; indeed, such solutions were quite unmanageable until I adopted this very simple expedient.

tains a large quantity of air. As soon, however, as this is expelled, the absorption becomes quite perfect, and is almost entirely confined to the Woulfe's bottle. After a short time, air is actually sucked slowly back through the Liebig's bulbs. As soon as this occurs, I begin to heat the generating flask, taking care, however, not to force gas through in the opposite direction. Quite at the close of the operation, the contents of the generating flask are boiled, the steam, of course, expelling all carbonic acid from the flask. As soon as the steam has fairly passed into the sulphuric acid for a few seconds, the lamp is removed; and the moment the sulphuric acid begins to rise in the pipette, the stop-cock into the generating apparatus is turned on. This allows air to enter, and prevents any regurgitation. During the process of boiling out, air will have begun to enter through the potash-apparatus. If we now suck a little air out of the potash apparatus, and then close up the aperture, the potash-solution will pretty rapidly suck the carbonic acid out of the remainder of the apparatus. The last traces are, of course, removed in the ordinary way—by sucking a little air through. It is then placed in cold water, allowed to stand in the balance case, and weighed, exactly as it was before the operation. The increase of weight represents the carbonic acid.

The first substance on which this determination was made was *butyric ether*. It was selected because Professor Wanklyn had himself prepared the ether, and obtained most satisfactory evidence of its purity. In this instance carbonic acid was determined by loss, a method as accurate as the direct weighing, but somewhat awkward, owing to the weight of the apparatus requisite. As I have now abandoned this method of determination, I do not think it necessary to describe the apparatus. In this instance equal volumes of the same solution were titrated; the one after it had been digested with the ether, the other in its original state. The following are the details of the titration of the unaltered solution:—

Weight of apparatus + unaltered chromic solution and oxalic acid solution, before the reaction	409·4495
Apparatus after the reaction	405·4115
Loss CO_2	4·0380

The other volume of solution was digested with 0·8163 grm. butyric ether, and constantly shaken; the temperature was very moderate, rather below than above 80°. After about two hours of this kind of digestion, the ether having completely disappeared, it was heated to 100° for a few minutes; the tube was then cooled and opened, and its contents, which had completely lost the smell of butyric ether, were transferred to the generating flask. Here they were heated in the water-bath, and a stream of air passed through them to remove any carbonic acid that might have been produced during the digestion; the amount of carbonic acid yielded by the action of the solution on excess of oxalic acid was then determined exactly as before. It yielded 2·7935 CO_2. Subtracting this from the quantity which the unaltered solution yielded (4·038 — 2·7935) we get 1·2445 of difference. This represents the amount of oxygen consumed by the butyric ether. It is, of course, in the form of carbonic acid. As one atom of oxygen corresponds to two of carbonic acid (16 O to 88 CO_2) $\frac{16}{88}$ or $\frac{2}{11}$ of this weight are due to the oxygen consumed by the butyric ether. Multiplying therefore 1·2445 by $\frac{2}{11}$ and by 100, and dividing by the weight of butyric ether employed, we obtain the percentage of oxygen consumed by the ether, viz., 27·71. The theoretical number, on the assumption that butyric and acetic acids are the sole products of this oxidation, is 27·58. We have therefore employed 100·47 instead of the 100 parts of oxygen. This ether was therefore free from all the impurities before enumerated. No portion of the acids produced had been attacked in any way by the bichromate solution. Indeed a more complete quantitative proof that the acids are not attacked it would be impossible to find.

The same solution was employed in each of the following oxidations. It contained about 7 per cent. of its *weight* of bichromate of potash. It was titrated with oxalic acid, the carbonic acid being estimated both by loss and by direct weighing. The two determinations gave respectively 7·5113 and 7·5251 as the percentage of carbonic acid liberated by the solution from excess of oxalic acid. These two differ as 100 and 100·17.

The next determination was made upon *propione*. This body it is possible to obtain in a state of chemical purity. It was produced by the oxidation of diethoxalic acid. The guarantees of its purity are given at full length in a former paper by Mr. Miles Smith and myself (p. 177 of this volume). 0·546

grm. of this substance was sealed up along with 54·428 of the before mentioned chromic solution, and digested at a low temperature with occasional shaking for about seven hours, and finally in the steam-bath for somewhat less than an hour. The contents of the tube were transferred to the generating flask, then heated in the water-bath, and a stream of air passed through them to remove any carbonic acid that might have been generated, then cooled, and the amount of unconsumed oxygen determined in the manner above described. The quantity of carbonic acid liberated was 2·4133. Calculating from the weight of the chromic solution employed and its known strength, how much carbonic acid it would have liberated had it been unaltered, we obtain the following result:—

$$100 : 7{\cdot}5182 :: 54{\cdot}428 : x$$
$$x = 4{\cdot}092\ CO_2.$$

Subtracting from this the amount of carbonic acid actually obtained, we find the difference due to the propione to be 1·6787.

$1{\cdot}6787 \times \frac{100 \times \frac{2}{11}}{{\cdot}546\ (\text{propione})} = 55{\cdot}901$, the percentage of oxygen consumed.

The equation

Propione.
$$C_5H_{10}O + O_3 = C_3H_6O_2 + C_2H_4O_2$$

requires 55·81 per cent. of oxygen. We have therefore consumed 100·16 instead of 100. As the propione was known to be chemically pure, we have here another proof not only of the accuracy with which these determinations may be made, but also of the stability of the acids of the acetic series.

The last instance of a determination of the oxygen consumed by a chemically pure organic body is that of *diethoxalic acid.*

·8827 grm. of this substance was sealed up with 67·126 grm. of the standard chromic solution, and gently heated for about 12 hours. The contents of the tube were treated precisely as in the case of the propione. The numbers obtained were—

Carbonic acid from unaltered solution, by calculation..	5·0467
Carbonic acid found after operation	2·6842
Difference	2·3625

$2{\cdot}3625 \times \frac{100 \times \frac{2}{11}}{{\cdot}8827} = 48{\cdot}66$, the percentage of oxygen consumed.

The equation

Diethoxalic acid.

$$C_6H_{12}O_3 + O_4 = CO_2 + H_2O + C_3H_6O_2 + C_2H_4O_2$$

requires 48·48 per cent. We have therefore consumed 100·37 instead of 100.

The oxidation of impure substances may sometimes be of value in affording information as to the nature of the impurity. The following oxidation of an impure specimen of *acetic ether* may serve as an example.

This ether had been prepared in the ordinary manner from pure alcohol, sulphuric acid, and acetate of potash; and dried over chloride of calcium. It had been titrated by Professor Wanklyn, who found that 100 parts of the ether saturated an amount of potash equivalent to 40·0 of potassium. Theoretically it requires 44·43. From this it follows that the ether contained 9·97 per cent. of impurity.

·6922 grm. were digested with 55·738 grm. of the standard chromic solution, and the carbonic acid which the latter liberated with oxalic acid after the digestion determined.

Amount of carbonic acid from unaltered solution by calculation.....	4·1905
Carbonic acid found after the operation	2·7230
Difference	1·4675

$1{\cdot}4675 \times \frac{100 \times \frac{2}{11}}{{\cdot}6922} = 38{\cdot}54$, the percentage of oxygen consumed.

The equation $C_4H_8O_2 + 2O = 2C_2H_4O_2$ requires 36·36 per cent. of oxygen. But as only 90·07 per cent. of the mixture was acetic ether, we subtract from the percentage obtained the percentage due to the acetic ether, viz., 32·75 per cent.; the difference, 5·79, is the amount of oxygen consumed by the impurity. Now as the only possible impurities are alcohol and water, we have here all the data necessary for determining their respective amounts; we have, in point of fact, 9·97 of mixed alcohol and water requiring 5·79 of oxygen. 100 parts of alcohol

would require 69·56 of oxygen. 100 parts of the impurity therefore would require 58·07 of oxygen. Then by the proportion, 69·56 : 58·07 : : 100 : x, giving $x = 83{\cdot}4$, we learn the percentage of alcohol in the mixture. The composition of the acetic ether was therefore as follows :—

Acetic ether	90·03
Alcohol	8·33
Water	1·64
	100·00

From the foregoing it is evident that we can make estimations of alcohol in this manner. The following is an example of the kind :—

·7036 grm. of spirit were digested with 64·03 grm. of the chromic solution, and the solution afterwards titrated as usual.

Amount of carbonic acid from unaltered solution by calculation.....	4·8139
Carbonic acid found after operation	2·4645
Difference	2·3494

$2{\cdot}3494 \times \frac{100 \times \frac{2}{11}}{{\cdot}7036} = 60{\cdot}7$ the percentage of oxygen consumed.

Alcohol requires 69·56 per cent. of oxygen ; therefore by the following proportion, we learn the percentage of alcohol in the spirit :—

69·56 : 60·7 : : 100 : x ; therefore $x = 87{\cdot}26$ percentage of alcohol.

In conclusion, I have to remark that I consider the investigation of the method of research by gradual oxidation as now complete. I am far from supposing that it will not undergo improvement, but it is now quite practicable, and not difficult of execution. It would give me great pleasure to see it employed by other chemists. I am convinced that by it, and by it only, shall we arrive at the true composition of the natural organic products, such as quinine, theine, morphine, the essential oils, &c.

It may be remarked that in the whole of the papers on gradual oxidation, no work has been done on bodies yielding high acids, the reason of which is, that the sources from which such bodies

may be obtained are all of such a nature that it is almost impossible to be sure of their purity, and in the investigation of a method nothing but pure substances are available.

XXII.—*On the Absorption and Dialytic Separation of Gases by Colloid Septa.*

By Thomas Graham, F.R.S., Master of the Mint.

[From the Philosophical Transactions for 1866.]

Part I.—Action of a Septum of Caoutchouc.

Mixed gases must differ considerably in diffusibility and specific gravity, in order to separate from one another to any great extent in their molecular passage into a vacuum through a porous septum, such as the plate of graphite or the walls of an unglazed earthenware tube. The agency of atmolysis is therefore very limited in parting the oxygen and nitrogen of atmospheric air—gases which differ so little in density from each other.

Substances existing in the liquid condition often admit of being separated much more fully than gases, by the proper use of dialytic septa in addition to the agency of liquid diffusion.

Evidently there cannot be anything like the dialysis of gases; for dialysis involves the passage of a substance through a septum composed of soft colloid matter, such as must be wholly destitute of open channels, and therefore be impermeable to gas as such. Still liquid dialysis may be imported into the treatment of gases, in consequence of the general assumption of liquidity by gases when absorbed by actual liquids or by soft colloids. Water when charged with air holds liquid oxygen and nitrogen in solution; and the latter substances then become amenable to liquid diffusion and dialysis, and so penetrate animal membrane in the act of respiration.

A considerable time ago Dr. Mitchell, of Philadelphia, discovered a power in gases to penetrate india-rubber in a thin sheet, or in the form of the little transparent balloons which Dr. Mitchell was the first to prepare from that substance. He

remarked in particular that such balloons collapse sooner when inflated with hydrogen than with atmospheric air, and still sooner when filled with carbonic acid; and he connected the latter fact with the observation that a solid piece of india-rubber is capable of absorbing its own volume of carbonic acid when left long enough in the pure gas. By means of a proper arrangement, Dr. Mitchell found that various gases passed spontaneously through the caoutchouc membrane, *when there was air on the other side*, with different degrees of velocity. "Ammonia transmitted in 1 minute as much as sulphuretted hydrogen in 2½ minutes, cyanogen in 3¼ minutes, carbonic acid in 5½ minutes, nitrous oxide in 6½ minutes, arsenietted hydrogen in 27½ minutes, olefiant gas in 28 minutes, hydrogen in 37½ minutes, oxygen in 1 hour and 53 minutes, carbonic oxide in 2 hours and 40 minutes." The rate of penetration of nitrogen appeared to be even slower than that of carbonic oxide.*

It will be observed that those gases penetrate most readily which are easily liquefied by pressure, and which are also "generally highly soluble in water or other liquids." The memoir of Dr. Mitchell was ably commented upon, shortly after its publication, by Dr. Draper of New York, who also added many new observations on the passage of both gases and liquids through membranous septa.† These early speculations, however, lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomena—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view.

Dr. Mitchell was led to infer, from a single casual observation, that solid rubber expands in volume when carbonic acid is absorbed—a result to be expected from the porosity of the

* "On the Penetrativeness of Fluïds," by J. K. Mitchell, M.D.—Philadelphia Journal of Medical Sciences, vol. xiii, p. 36; or Journal of the Royal Institution, vol. ii, pages 101 and 307: London, 1831.

† A Treatise on the Forces which produce the Organization of Plants, with an Appendix containing several Memoirs on Capillary Attraction, Electricity, and the Chemical Action of Light, by John William Draper, M.D.

mass, then assumed in explanation of the penetrativeness of gaseous fluids. But on placing 50 grms. of thin sheet rubber, 0·6 millim. in thickness, in carbonic acid over mercury, it was seen that the rubber gradually absorbed 0·78 volume of gas in twenty-four hours at 15°, of which 0·7 volume was taken up in the first hour. The mass of rubber was previously measured with care by the displacement of mercury in a specific-gravity bottle, and again when the rubber was charged with carbonic acid; it gave the same displacement of mercury within a hundredth of a gramme. No measurable change in the bulk of the rubber, therefore, had occurred. It may be added that the absorbent power of vulcanized rubber for carbonic acid appears to be less than that of rubber in its natural state, being found only 0·57 volume in a comparative experiment.

The penetration of rubber by gases may be illustrated by their passage into a *vacuum*, as well as into an atmosphere of another gas in Dr. Mitchell's experiments. The diffusiometer, consisting of a plain glass tube of about 22 millims. in diameter and nearly a whole metre in length, closed at the upper end by a thin plate of stucco and open below, is taken advantage of in such experiments. A thin film of rubber from a small balloon is stretched over the upper end of the tube, where it is supported by the stucco plate, bound with copper wire, and cemented at the edges in contact with the glass with gutta-percha softened by heat. If the tube be now filled with mercury and inverted, a Torricellian vacuum is obtained above, into which the air of the atmosphere gradually penetrates, passing through the film of rubber and depressing the mercurial column in the tube. In order to compare the penetration of different gases, a hood of thick vulcanized rubber, provided with a small entrance- and exit-tube for gas (such as is often used in gas experiments), is placed over the upper end of the diffusiometer described, and cemented to it by means of fused gutta-percha. The gas to be operated upon can thus be conveyed from the apparatus in which it is generated, or from a gasometer in which the gas is stored, into the hood or upper chamber of the diffusiometer, and the excess of gas supplied may be allowed to escape into the atmosphere by the exit-tube of the hood. The stucco plate used as a support to the film of rubber is so highly porous as not to add sensibly to the resistance experienced by the gases in passing through the rubber,

and, having no absorbent power of its own, may be left entirely out of consideration.

A comparison was made of the passage through the rubber film, on the same day, of carbonic acid, hydrogen, oxygen, and nitrogen; barom. 773 millims., therm. 23° to 23°·5 C. The time during which the mercurial column fell in the diffusiometer from 748 to 723 millims. was noted in seconds, and also from 723 to 698 millims. The gases were all carefully dried.

TABLE I.—*Passage of Carbonic Acid in seconds.*

Height of mercurial column in diffusiometer.	Experiment 1.	Experiment 2.	Experiment 3.
millims.			
748			
723	107″	102″	102″
698	143	138	138
	250	240	240

The passage of carbonic acid thus exhibited will be found to be considerably more rapid than that of hydrogen and the two other gases which follow:—

TABLE II.

Height of mercurial column in diffusiometer.	Passage in seconds, of Hydrogen.		of Oxygen.		of Nitrogen.	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.
millims.						
748						
723	277″	270″	545″	554″	1413″	1428″
698	316	323	727	722	1832	1850
	593	593	1272	1276	3245	3278

A single experiment, made at the same time on the passage of atmospheric air, gave times of 1318″ and 1524″ for the two stages, or 2842″ for the whole fall. The time of penetration of

air is therefore intermediate between that of oxygen and nitrogen entering singly.

Although such numbers do not possess the close uniformity which appears in diffusion- and transpiration-experiments, for reasons which will immediately appear, yet they give a comparative estimate of the penetrativeness of the different gases through rubber, which may be available for some practical purposes.

Upon another occasion carbonic oxide and marsh-gas (CH_4) were introduced into the comparison, the same film of rubber remaining upon the diffusiometer; barom. 768 millims., therm. 19°·5 C.

TABLE III.

Height of mercurial column in diffusiometer.	Passage in seconds,								
	of Carbonic oxide.		of Hydrogen.		of Carbonic acid.			of Marsh-gas (CH_4).	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 1.	Expt. 2.
millims.									
748									
723	1620″	1631″	435″	434″	125″	119″	117″	803″	821″
698	1920	1924	505	511	170	169	172	1009	1045
	3540	3555	940	945	295	288	289	1812	1866

The results may be summed up by deducing the times in which a constant volume of the various gases is transmitted by the rubber, the time of passage of carbonic acid, which is the shortest, being taken as unity for the sake of comparison.

Penetration of rubber by equal volumes of Gas.

	Time.
Carbonic acid	1
Hydrogen.....	2·470
Oxygen.....	5·316
Marsh-gas (CH_4).....	6·326
Atmospheric air	11·850
Carbonic oxide.....	12·203
Nitrogen	13·585

Or, with the times taken equal, the volume of each gas which passes then expresses the velocity of penetration.

Penetration of rubber in equal times.

	Velocity.
Nitrogen	1
Carbonic oxide.....	1·113
Atmospheric air	1·149
Marsh-gas (CH_4).....	2·148
Oxygen.....	2·556
Hydrogen.....	5·500
Carbonic acid	13·585

Considering the circumstances in which the gases pass through the sheet of rubber into a vacuum, it is not to be expected that any relation will be found among the preceding numbers, as between the co-efficients of diffusion in gases. The first absorption of the gas by rubber must depend upon a kind of chemical affinity subsisting between the material of the gas and substance of rubber, analogous to that attraction which is admitted to exist between a soluble body and its solvent, conducing to solution. Carbonic acid being soluble in ether and volatile oils, it is not wonderful that it is also dissolved by the hydrocarbons of rubber. The rubber being *wetted through* by the liquefied gas, the latter comes to evaporate into the vacuum, and reappears as gas on the other side of the membrane. Now it is known that such evaporation is the same into a vacuum and into another gas, being equally gas-diffusion in both circumstances. It is not indispensable, therefore, to have a vacuum on one side of the rubber membrane as in the experiments detailed above. A foreign gas will answer for the vacuum, as in the experiments of Dr. Mitchell.

The numbers for the velocity of passage of the different gases in the last table may be taken also as representing not remotely the relative absorption and liquefaction of the various gases by the substance of rubber.

The passage of gases through rubber is also illustrated by the rapid collapse of the little balloon when filled with carbonic acid gas, or even with hydrogen, or with marsh-gas, as compared with atmospheric air. The converse fact is observed when the inflating gas is pure nitrogen: then the balloon is found to become further distended after a few hours, in consequence of more oxygen entering from the atmosphere without, than of nitrogen escaping from the balloon during the same time; while

the composition is being equalized on both sides of the membrane, and the gas within the balloon is finally of the same composition as the external air. A rubber balloon filled with nitrogen was found, when roughly gauged, to increase in diameter from 132 to 136 millims. in the course of twenty-four hours. On the other hand, a balloon filled with pure oxygen fell in the same time from 150 to 113 millims. in diameter.

In forty-eight hours a balloon filled with hydrogen, 154 millims. in diameter contracted to 87 millims., and then contained 250 cub. centims. gas, of which 53 cub. centims. were absorbed by pyrogallic acid and potash, showing the presence of 21·2 per cent. of oxygen, or sensibly the same proportion as in the external atmosphere.

If the upper end of a diffusiometer be closed by a thin sheet of rubber, and the instrument standing over mercury be filled with hydrogen gas, a contraction is observed to take place slowly, but to a greater extent ultimately than could be due to the diffusion of hydrogen as a gas. Beginning with 249 volume-divisions of gas in the tube, the rise of the mercurial column or reduction of volume, was 1·5 division in the first hour, 1·5 division in the second hour, 2·0 in the third hour, 3 in the fourth hour, and 51 divisions in the first twenty-four hours taken together. Then the rise in the following successive days was 42, 59, 37, 29, 13, 5, 1, 0·5, 0·5 (in two days), and 0·0, the original volume of 249 volumes of hydrogen being finally replaced by 53 volumes of atmospheric air; barom. 747 millims., therm. 21°·1. The ultimate replacing volumes are here as 1 to 4·7. In gas-diffusion they are as 1 to 3·8.

A balloon filled with air subsided in forty-eight hours from 150 to 147 millims. in diameter, from the mechanical effect alone of the elasticity of the membrane in compressing the enclosed gas. These little balloons vary from 0·75 to 1 grm. in weight. Supposing the form to be truly spherical, a balloon of 150 millims. in diameter would have a surface of 0·0706 square metre (5·905 inches in diameter and 0·08454 square yard of surface). Supposing the balloon to be 1 grm. in weight, the thickness of the membrane will be $\frac{1}{76.858}$ of a millim., with a specific gravity = 1, or $\frac{1}{76.01}$ of a millim., with a specific gravity = 0·93, the admitted density of pure rubber. This last is a thickness of $\frac{1}{1930.8}$ of an inch, or it would require nearly 2,000 of such films, laid upon each other, to form the thickness of a single inch.

Yet such a film of rubber appears to have no porosity, and to resemble a film of liquid in its relation to gases—differing entirely in this respect from a thin sheet of paper, graphite, earthenware, or even gutta-percha, as will appear hereafter. These last enumerated bodies appear all to be pervaded by open channels or pores, sufficiently wide to allow gases to be projected through by their own proper molecular movement of diffusion. But liquids and colloids have an unbroken texture, and afford no opportunity for gaseous diffusion. They form even in the thinnest film an impervious barrier to gas.

The penetration of rubber is much affected by temperature, and apparently in two different ways at the same time. An increase of temperature no doubt renders all gases less easily liquefied by pressure, and consequently less considerably absorbed by any liquid or colloid. But such an influence of heat appears to be counteracted in rubber by the tendency of that colloid to become more soft when heated, and to acquire more of liquid and less of solid properties. Certainly the rubber film becomes more and more permeable to gases as the temperature is elevated, within a moderate range. This was distinctly observed in operating with silk cloth varnished on one side with rubber, such as is sold as a waterproof material. Without anticipating a detail of the experiments, it may be stated in general terms that the same specimen of rubber was penetrated by air from the atmosphere passing into a vacuum, at the following rates per square metre of surface :—

At 4° C., by 0·56 cub. centim. of air in 1 minute.
At 14° C., by 2·25 „ „ „
At 60° C., by 6·63 „ „ „

The volumes of gas are all reduced to barom. 760 millims. and therm. 20° C.

Such numbers are probably not strictly constant ; for it appears that the effect of temperature upon rubber is much influenced by the length of time that the temperature is continued, the change in degree of softness with change of temperature requiring hours, or even days, fully to complete it. The rigidity of rubber under cold and its softening under warmth are well known to take place in a slow and gradual manner.

With the softening of rubber by heat, the *retentive* power of

that substance for gases appears to be modified. Soft rubber, first charged with carbonic acid at 20°, and then made rigid by cold, appeared to lose its carbonic acid when afterwards freely exposed to air, less rapidly than the same rubber equally charged but exposed from the first in its soft condition. The quantity of carbonic acid retained in the former case was 10·76 per cent., and in the latter 7·08 per cent. of the volume of the rubber, after a similar exposure of forty-eight hours. This point, although not sufficiently examined, is alluded to here on account of the analogy which appears to hold between rubber and the malleable metals in the power to absorb a gas when they are softened by heat, and to retain the same gas with great tenacity when they are afterwards made rigid by cold.

The condensation of oxygen gas by masses of solid rubber punched out of a block was made the subject of observation, by placing 50 grms. of that substance within a jar of oxygen standing over mercury during a period of several days. From the rubber afterwards there was extracted, by the action of a vacuum continued for twenty-one hours, 6·21 cub. centims. of gas; of which 3·67 cub. centims. were oxygen, 0·14 carbonic acid, and the remainder chiefly nitrogen. Taking the bulk of the rubber at 53·8 cub. centims., the oxygen absorbed amounts to 6·82 per cent. of the volume of the rubber. Oxygen then may be regarded as fully twice as soluble in rubber as the same gas is in water at the ordinary temperature. No experiment was made at a higher temperature; but as the penetrativeness of rubber is much increased by heat, the presumption is that the solubility of gases in rubber is increased in the same degree.

More than one attempt was made to identify the presence of free hydrogen in the substance of rubber after being kept in that gas for some time, but with a negative result. The absorbed hydrogen may be too easily dissipated, owing to its extreme volatility.

Dialytic separation of Oxygen from Atmospheric Air, (1) by means of other gases, (2) by means of a vacuum.

1. A balloon of rubber filled with *hydrogen* and exposed to the atmosphere, gradually loses the former gas, which is finally replaced by a considerably smaller volume of air, presenting a deceptive resemblance to the diffusion of hydrogen gas into air.

When the progress of the entrance of air was observed at different stages of the exchange, it appeared that after three hours, when the balloon had fallen from 150 to 128 millims. in diameter, the composition of its contents was—

Oxygen	8·98	41·6
Nitrogen	12·60	58·4
Hydrogen	78·42	
	100·00	100·0

Setting aside therefore the hydrogen still remaining, the balloon now contained a portion of a mixture of oxygen and nitrogen in the proportion of 41·6 volumes of the former to 58·4 volumes of the latter. This was the largest proportion of oxygen to the nitrogen observed; for the former gas has a tendency to flow back again to the external atmosphere when the hydrogen becomes small in volume; and the proportion of oxygen becomes eventually no higher than 21 per cent. of the whole gases remaining in the balloon, including the hydrogen. Thus, after six hours, the proportion of oxygen was 33·63 to nitrogen 66·37 volumes, and after twenty-four hours oxygen 26·48 to nitrogen 73·52 volumes, the hydrogen constantly diminishing at the same time.

The entrance by infiltration of atmospheric air into a balloon of rubber inflated with *carbonic acid* gas brings us still nearer to a practical dialytic separation, as the carbonic acid can be withdrawn entirely by means of caustic alkali, after a certain time has elapsed, and the infiltered air enriched with oxygen can be dealt with by itself. A balloon containing carbonic acid, when placed in the atmosphere, was reduced in four hours from 160 to 90 millims. in diameter, and it had now acquired 199 cub. centims. of gas not dissolved by alkali. This gas was capable of reviving the combustion of wood burning without flame, and was found to consist of

Oxygen	37·1 vols.
Nitrogen.....	62·9 „
	100·0

To produce this concentration of oxygen, it is quite necessary that the operation be interrupted at an early stage, as was done

in the last experiment; otherwise the oxygen diminishes again in proportion to the nitrogen, falling at last to the normal proportion of 21 per cent. as in the external air. Thus a balloon inflated by carbonic acid to 150 millims. in diameter, was found to lose nearly all its carbonic acid in the course of twenty-four hours. It gave 150 cub. centims. of gas after treatment with caustic potash. This was air of the composition,

Oxygen	22·6
Nitrogen.....	77·4
	100·0

and exhibited therefore no material augmentation in the proportion of oxygen.

It may be inferred, from the familiar fact that air dissolved in water contains so high a proportion as 30 per cent. of oxygen, that if carbonic acid gas were divided from atmospheric air by a film of *water*, the former gas would come to be charged through the film with air bearing the same high proportion of 30 per cent. of oxygen. But it is not easy to imitate this experiment unless the dividing film is supported by a membrane of some sort. The air from the atmosphere, which entered a fresh ox-bladder preserved humid and inflated with carbonic acid, was found to possess 24·65 per cent. of oxygen to 75·35 of nitrogen, which is but a small increase in the proportion of oxygen. But the thickness of the membrane here was too great, and other circumstances of the experiment were unfavourable.

A balloon of rubber inflated to 150 millims. in diameter with carbonic acid was submerged in water, at 22° C., for forty-eight hours. Only a small portion of carbonic acid remained in the residual gas, which, after being washed with potash, consisted of—

Oxygen.....	25·77
Nitrogen	74·23
	100·00

2. With the colloid septum properly supported, as by a stucco plate in the diffusiometer covered by a film of rubber (p. 241), a considerable separation of mixed gases can be effected. The constituents of atmospheric air appear to be carried through a

film of rubber into a vacuum, nearly in the same relative proportion as the same gases penetrate singly (p. 240). The velocities of nitrogen and oxygen passing separately were observed to be as 1 to 2·556, and hence by calculation,

Oxygen	21 × 2·556	= 53·676	....	40·46
Nitrogen	79 × 1	= 79	....	59·54
				100·00

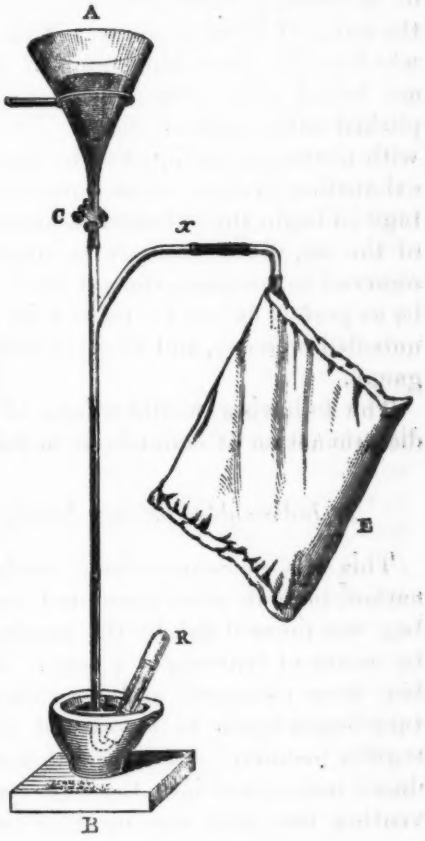
Hence air dialyzed by the rubber septum should consist of 40·46 oxygen and 59·54 nitrogen in 100 volumes. Now air from the atmosphere was found to enter the vacuum of the 48-inch diffusiometer-tube, through a disc of rubber 22 millims. in diameter, to the amount of 3·48 cub. centims. in twenty-one hours, under the pressure of the atmosphere; therm. 23° to 24° C. Of the 3·48 cub. centims. of gas so collected, 2 cub. centims. were absorbed by pyrogallic acid and potash, representing 42·53 *per cent. of oxygen* in the dialyzed air. Here the gas was transferred from the diffusiometer for examination by depressing the diffusiometer in mercury, and using a very narrow tube of rubber as a gas-siphon communicating between the gas in the diffusiometer and a jar inverted in the mercurial trough. The elastic tube is first filled with mercury, and, being of considerable length, a portion of it is drawn repeatedly through the fingers, so as to throw the mercury and aspirated gas into the collecting receiver. The transference of gases in such circumstances may also be effected with much advantage by means of the vacuum-tube invented by Dr. Hermann Sprengel, as will immediately be shown.

The process of dialytic separation by means of a rubber septum may be varied in three points—(1) in the condition of the rubber septum, which may be a film of rubber formed from caoutchouc varnish as well as distended sheet rubber; (2) in the nature of the support given to the septum, which may be a backing of cotton cloth or of silk (common waterproof cloth prepared by means of caoutchouc varnish, in short), as well as a plate of stucco, earthenware, or wood; and (3) in the means had recourse to for sustaining a vacuum, or at least a considerable degree of exhaustion, on one side of the dialytic septum, while atmospheric air, or any other gaseous mixture to be dialyzed, has access to the other side of the same septum. Or the

air to be dialyzed may be compressed on one side of the septum, and left of the usual tension on the other side, inequality of tension on the two sides of the septum being all that is required to induce penetration.

The pneumatic instrument of Dr. Sprengel (fig. 1) is peculiarly applicable to researches of the present kind. Indeed without the use of his invention some parts of the inquiry would have been practically impossible.* The instrument was originally offered by the inventor as the means of producing a vacuum, or as an air-pump. But by bending the lower end of the straight fall-tube, the instrument may be further made to deliver gas into a receiver, and be used with advantage as the means of transferring small volumes of gas from one vessel to another.

Fig. 1.



While the mercury in the funnel A is allowed to flow downward into the barometer-tube CB, of 2½ millims. in diameter, by relaxing the clamp upon the adapter tube of rubber at C, a connexion is also made with the close receiver to be exhausted, such as an air-tight bag E, by means of the branch-tube *x*. The air in E, gaining access to the Torricellian vacuum, is swept on by the falling mercury, and delivered below into the small gas-receiver R, previously filled with mercury, and inverted over mercury in the mortar B below. The principal difficulty in

* Researches on the Vacuum, by Hermann Sprengel, Ph.D., Chem. Soc. J, [2], iii, 9 (January, 1865).

obtaining a good vacuum in E by means of this apparatus arises from the necessity of joining the glass tubes in more than one place by means of adapter-tubes of rubber. The directions given by Dr. Sprengel on this point require to be closely followed:—"The connexions between the glass tubes are made of well-fitting black vulcanized caoutchouc tubing, sold under the name of French tubing. This is free from metallic oxides, which render the tubing porous. Besides this all these joints are bound with coils of copper wire, which is easily accomplished with a pair of pliers." The joints should also be coated with gutta-percha liquefied by heat, or with fused rubber. An exhausting syringe, or air-pump, may often be used with advantage to begin the exhaustion, and to withdraw the greater bulk of the air, if the receiver is large, the Sprengel tube being reserved to complete the exhaustion. The vacuum appears to be as perfect as can be formed in a barometer-tube filled with unboiled mercury, and to come within 1 millim. of the barometric gauge.

The following modifications of the experiment exhibit the dialytic action of caoutchouc in its various forms.

1. *India-rubber between Double Cotton Cloth Vulcanized.*

This was a common elastic carriage-bag 18 inches by 15. The surface of both sides amounted to 0·3482 square metre. The bag was pressed flat by the hands, and still further exhausted by means of Sprengel's tube. After all the contents of the bag were extracted and the collapse complete, the Sprengel tube began again to throw out air in a slow but exceedingly regular manner. A small portion of sawdust, or of sand, introduced beforehand into the bag, appeared to be useful in preventing the sides coming together too closely, but was not essential. The air thus extracted from the bag in one hour amounted to 15·65 cub. centims., or sensibly 1 cubic inch; therm. 23° to 24° C. Such dialysed air, from three successive experiments of one hour each, contained 38, 40·3, and 41·2 per cent. of oxygen, the inferior proportion of oxgen in the earlier experiments being no doubt due to a small residue of undialysed air remaining in the bag before exhaustion. This dialysed air rekindled glowing wood, so as to illustrate the direct separation of oxygen gas from atmospheric air. For the purposes of com-

bustion, it may be viewed as air from which one-half of the inert nitrogen has been withdrawn.

It will be convenient to express the permeability of the colloid septum with uniform reference to a square metre of area, and to an hour, or to a single minute of time. Here, for a square metre of cloth, the passage of air amounted to 44·95 cub. centims. (3 cubic inches nearly) per hour, or to 0·749 cub. centim. per minute.

The view which the observation suggests of the nature of such air-tight fabric is, that it may be truly impenetrable to air when the composition and tension of the air are the same on both sides of the cloth; but it is penetrable when a vacuum or a reduced state of tension is maintained on one side of the cloth and not on the other. The compression of the air confined in a bag would no doubt have a similar effect, and then the flow would be in an outward direction. But there is no evidence of a porous structure in the varnished cloth. The gases of atmospheric air would pass through actual openings according to the law of gaseous diffusion, which favours the nitrogen or lighter gas, while it is the oxygen which is found to pass through the material most readily in these experiments. The imbibition of the liquefied gas by the substance of the rubber, with the subsequent evaporation of this liquid into the vacuum on the other side, is all the explanation required.

2. *Vulcanized India-rubber Tubing.*

A stout caoutchouc tube with an external diameter of 13 millims. (half an inch), an internal diameter of 9 millims., thickness of 2 millims., and length of 3·658 metres (4 yards) was exhausted, one end being closed and the other end connected with the Sprengel pump. The gas collected in thirteen hours amounted to 11·25 cub. centims.; therm. 20° to 23° C. This gas contained 37·8 per cent. of oxygen. The gaseous penetration is not great in so thick a tube, and there is reason to fear the influence of gaseous diffusion to a small extent. The admission of air would be equally sensible if the tube were occupied by coal-gas, or any other foreign gas, instead of being vacuous. As the inner surface of the tube amounted to 0·1034 square metre and the passage of air to 0·8653 cub. centim. per hour, the passage for a square metre would be 8·37 cub. centims. per hour,

or 0·14 cub. centim. per minute. The rate of penetration through the tube-walls appears to be one-fifth of what was found for the rubber cloth.

3. *Sheet Rubber*, 1 *millim. in Thickness.*

Although an increased thickness was no doubt attended by slowness of passage, it was of interest to observe whether the proportion of oxygen per cent. might not at the same time be varied. The sheet used was still, however, as thin as the manufacturer could succeed in cutting from a solid cylinder of wrought rubber by the usual method. The rubber was not vulcanized. The sheet of rubber was made into a bag having 0·149 square metre (231 square inches) of surface, a double thickness of felted carpet being placed within the folds of rubber. A glass quill tube, cemented to the bag, communicated with the interior of the cavity, and was connected at the other end with Sprengel's tube. After the first exhaustion of the gaseous contents of the bag, for which the aid of an exhausting syringe or air-pump is useful, air continued to infiltrate through the sheet rubber, but very slowly. Of the dialysed air 11·45 cub. centims. were collected in four hours. This air contained 41·48 per cent. of oxygen, with a sensible trace of carbonic acid. The penetration for a square metre amounts to 19·2 cub. centims. of air per hour, or 0·32 cub. centim. per minute.

The same bag, left exhausted for eighteen hours, was found afterwards to yield at once 41·6 cub. centims. of air, containing 40·3 per cent. of oxygen, which had accumulated in the cavity of the bag: therm. about 20° C.

From a larger bag of similar thin sheet rubber, having a surface of 640 square inches, distended by ten or twelve ounces of sawdust, 21·35 cub. centims. of dialysed air were obtained in one hour; barom. 761 millims., therm. 19°·5 C. This dialysed air appeared to consist of

Oxygen.....	41·80
Carbonic acid	0·94
Nitrogen	57·26
	100·00

It does not appear, then, that the increased thickness of the rubber septum tends to increase the proportion of oxygen in

the dialysed air, while this thickness causes the passage to be proportionally slower. The oxygen appears to attain, but never to exceed, at 20° C., the proportion of 41·6 to 58·4 nitrogen.

The thick rubber brings notably into view the carbonic acid of the air. The small proportion of this gas in air is probably increased in all experiments with the rubber septum, however thin. It was observed to rise so high in a small crowded room, as to negative the inflaming action of the oxygen on smouldering wood. But rubber appears to have a power to charge itself gradually from atmospheric air with about half per cent. of its volume of carbonic acid. This carbonic acid, accumulated in thick sheet rubber, appears again to be carried on by the other gases imbibed in a dialytic experiment.

4. *Thin Balloons of India-rubber.*

These little balloons were made available for the dialytic passage of air into a vacuum by filling them with sifted sawdust through a funnel, an operation which requires some address. The balloon collapsed upon the sawdust, which formed an interior ball, the sides of rubber still retaining a thickness of about one-fiftieth of a millimetre. The rubber is not vulcanized. Such a ball, of which the original rubber weighed 0·76 grm., still remained 95 millims. in diameter after the air was exhausted. It was found, when exhausted, to admit 19·6 cub. centims. of dialysed air in forty-one minutes; barom. 579 millims., and therm. 19° C. The same air possessed 41·32 per cent. of oxygen. The ball had a surface of 0·0283 square metre, and it dialyzed 0·48 cub. centim. of air in one minute. For a square metre of surface this is a passage of 16·9 cub. centims. per minute. The passage therefore is about fifty times as fast as through a sheet of rubber of 1 millim. in thickness, while the high proportion of oxygen is sensibly the same. Such a ball was found to dialyse air in the same manner for more than a month, if protected from mechanical injury.

Three such balls, each containing twenty-three ounces of sifted sawdust, were made to act together, by connecting them with three dependent branches from the same horizontal glass tube. The horizontal tube was connected at one end with an

ordinary air-pump which produced a good vacuum by thirty or forty strokes of the piston. The other end of the horizontal glass tube was attached to a good Sprengel apparatus of the largest admissible size, constructed by Messrs. Elliot of the Strand. It was found, however, that the dialysed air entered rather more rapidly than it could be extracted by a single Sprengel apparatus. This was at the rate of 5 cub. centims. in one minute; therm. about 20° C. The dialysed air contained 40·5 per cent. of oxygen.

The greatest amount of aërial dialysis per square metre was obtained by means of a rubber bag, larger than usual, and weighing 1·55 grm. When filled with the sawdust and exhausted, this bag still remained of 143 millims. in diameter, and with a surface therefore of 0·0642 square metre. The air which passed through amounted to 17·05 cubic centims. in ten minutes; therm. about 20°. This air gave 40·7 per cent. of oxygen. For a square metre of surface, this is the passage of 26·5 cub. centims. per minute, the highest which has as yet been observed.

In the thin transparent envelope of the little balloon of rubber we have a colloid substance in the most favourable form yet applied to the dialysis of mixed gases. But there is still much room for improvement in the mode of using the thin septum in question. The balls are apt to contract considerably, owing to their elasticity, in the operation referred to, of filling them with sawdust; their walls become at the same time thicker and less quickly pervious. A mode of destroying the elasticity of the membrane when in its most attenuated condition, so that the balloon might be cut open and the membrane spread out without shrinking, would be very useful. Instead of depending upon the interior support of sawdust, the membrane could then be stretched over a more convenient frame to support it, of thin porous deal, of unglazed earthenware, and even of a felted fabric, or several thicknesses of unsized paper supported by a slight frame, so as to form a hollow cavity that admitted of being exhausted of air. The attention of manufacturers of rubber might be advantageously directed to the preparation and proper support of the thinnest possible septa of that material.

The varnish of rubber which appeared to offer the best septum on drying, was a thin solution of rubber in 200 times

its weight of chloroform. Four or five coats of this varnish required to be applied to a surface of wood, or of unglazed earthenware, to form an air-tight envelope. The film appeared to exceed in thickness the rubber balloons, and it dialysed air less rapidly. But a better result may be expected at the hands of experienced manufacturers.

The thin rubber membrane of the balloons was stretched over the ends of glass tubes already closed with a plate of porous stucco—and also over the mouths of small glass bulbs or osmometers, closed with a disk of porous wood or of unglazed earthenware, presenting a surface of one-hundredth of a square metre. The membrane of the balloon could only be applied while double; but after the covering was securely bound to the glass and cemented with fused gutta-percha at the edges, the outer coating was torn off, so as to leave only a single thickness of rubber as the dialytic septum. A bulb of the kind described, when exhausted by a Sprengel pump, gave afterwards 16·36 cub. centims. of dialysed air in two hours, containing by analysis 41·3 per cent. of oxygen, therm. 23° C.; in the following two hours, 17·35 cub. centims. of air, containing 42·6 per cent. of oxygen. This last is at the high rate, for a square metre of surface, of 14·46 cub. centims. per minute.

5. *Silk Cloth varnished with rubber on one side, slightly vulcanised.*

This is a thin but close silk fabric, much used for waterproof garments. It appears also to be employed, when dyed of a fancy colour, in the preparation of artificial flowers and for other purposes. The silk cloth is of a single thickness; and the coating of rubber, which is of a black colour, appears on one side only. It is a much superior material to the ordinary cotton fabrics, which are double, with the two varnished sides pressed together, and is much more to be depended upon for being sound and free from pores than the "waterproof" cotton cloth. The silk cloth, however, should always be tested by examining air dialysed by means of it. If the proportion of oxygen falls below 40 per cent., the silk is unsound at one or more spots. These spots may generally be discovered by wetting one side of the silk with a sponge and observing where the passage of water is indicated by a visible stain on

the other side. The defective spot may be covered by a small disk of sheet rubber applied warm to the surface. Such varnished silk, although not the most rapid in its dialytic action, was more convenient in use than any other septum hitherto tried.

The varnished silk stretched over a disk of porous earthenware (for support) closing the mouth of the small glass bell-jar or osmometer, which has an opening of one-hundredth part of a square metre, gave 10 cub. centims. of dialysed air in one hour, containing 42·2 per cent. of oxygen; barom. 767 millims., therm. 23°·5. For a square metre of surface this is a passage of 2·77 cub. centims. of air per minute.

A small bag, useful for experimental purposes, was constructed of a portion of the same varnished silk, 0·53 metre in length by 0·27 metre in width, which had therefore a surface of 0·143 square metre. The varnished side was turned inwards. Between the folds of the silk was placed a double thickness of common felt carpet or a piece of wadding, so as to occupy the interior of the bag. A glass quill tube also entered the bag to the depth of a few inches, and projected as much outside, so as to admit of being connected, by means of a sound adapter tube of French rubber, with a Sprengel pump, as shown in figure 1 (page 247). The edges of the silk cloth were cemented round by caoutchouc varnish, to a depth of 10 millims., so as to close the bag; and care was taken also to cement the glass tube well to the edges of the bag. When the silk bag is exhausted of air, it remains nearly flat, and feels hard like a piece of cardboard. Such an *air-dialyser* is further improved by interposing a strong glass flask or bottle, of one or two litres in capacity, between the bag and the pump, so that both are exhausted of air at the same time. The flask must be strong enough to bear the full pressure of the atmosphere without breaking. An auxiliary air-pump, to produce the first exhaustion, cannot well be dispensed with where the space to be made vacuous is so considerable; the Sprengel tube is brought into action afterwards. The advantage gained by the vacuous flask, and even by the thick wadding placed within the bag, is that they form a magazine in which the dialysed air can be allowed to accumulate for several hours or a whole day, and from which the air may afterwards be drawn quickly by the Sprengel tube for the purpose of experiment. A narrow

glass receiver tube, which can be closed by the thumb, may be used to take 5 or 6 cub. centims. for an observation on the inflammation of a chip of wood in the highly oxygenated air. When the proportion of oxygen is under 33 per cent. the wood is not rekindled; but in the ordinary action of this dialyser the oxygen is seldom found under 40 per cent. The best result is obtained when the exhaustion is within half an inch of the barometric vacuum. When the pressure was allowed to fall to one-half or one-third of an atmosphere, the proportion of oxygen was lessened by 2 or 3 per cent.

The action of heat and cold on the penetrability of rubber is considerable, as has already been stated. Operating with the dialysing-bag described, without any intermediate flask, the volume of air collected in twenty minutes was 6·35 and 6·57 cub. centims. in two consecutive experiments; barom. 760 millims, therm. 20°. For a square metre the rate is 2·22 and 2·29, average 2·25 cub. centims. per minute. The proportion of oxygen was, in the first experiment 42·5, and in the second 41·66 per cent.

When the same dialysing-bag was kept at a temperature of 60° C., the volume of air collected in seven minutes was 6·22 and 7·06 cub. centims. For the square metre this amounts to 6·21 and 7·05, mean 6·65 cub. centims. per minute. The passage of air through rubber is therefore almost exactly three times as quick at 60° as at 20° C.

Again, the dialysing-bag was kept at 4° C. by being surrounded by ice and salt. The air now collected in seventy-two minutes was 5·78 and 5·77 cub. centims. in volume—for a square metre 0·56 cub. centim. per minute. The passage of air through rubber thus appears to be four times as slow at 4° C. as it is at 20°. The proportion of oxygen in the dialysed air increased at the same time. In the two portions of air collected at 4° the oxygen was 46·75 and 47·43 per cent. The increase of oxygen at a low temperature was confirmed in other experiments; but it appeared at the same time that the rubber was liable to acquire a true porosity to a slight extent when retained for some hours about 0° C. The rubber then allowed air to pass through it containing no more than 28 or even 23 per cent. of oxygen, and in volume still very small. The rubber has become rigid by the cold, and is now acting feebly as a porous substance, allowing a little gas-diffusion to take place through its

substance. Such a condition, which is accidental to caoutchouc at a low temperature, appears to be constant with gutta-percha, a harder material, at 20° C., and even higher temperatures.

A large bag of varnished silk with a surface of 1·672 square metre (two square yards) was found still more convenient. It was, however, rather beyond the exhausting-power of the largest Sprengel pump. It yielded in eight minutes, without any collecting-flask, 22, 21·55, and 21·5, mean 21·68 cub. centims. This was a supply of 2·71 cub. centims. per minute, and was at the rate, for a square metre, of 1·62 cub. centim. per minute. The supply would have been about a half more if the dialyzed air had not gained upon the pump. The air of the first and last observations contained respectively 41·89 and 41·85 per cent. of oxygen.

The usual proportion of oxygen in air dialysed by rubber appears to be about 41·6 per cent.; and it may be described as atmospheric air deprived of one-half of its usual proportion of nitrogen. A single dialysis of air therefore carries the experimenter already halfway from air to pure oxygen as the final result. But the gain by a second dialysis could not be so great, as it would only withdraw one-half of the nitrogen that remained after the first operation, a third dialysis one-half of the nitrogen remaining after the second operation, and so on—each step of the concentration of the oxygen being obtained at a greater cost than the last, and the best conceivable result being only a good approximation. The practical problem which is suggested by the air-dialyser is, to attain the means on a large scale of reducing to one-half, or so, the proportion of nitrogen in atmospheric air, to be applied to certain useful purposes.*

* In all the observations above related the air was under the pressure of the atmosphere on one side of the rubber, and was drawn through the latter into a vacuous, or nearly vacuous, space on the other side. It is very important to maintain a good vacuum, or at least a considerable amount of exhaustion, for the purpose of aspiration, for the permeating air appears to be not only reduced in volume in proportion as the aspirating force is reduced, but the proportion of oxygen to the nitrogen is also diminished in a similar ratio. While with an aspiration of $0^{m}{\cdot}763$ (or a full atmosphere) the proportion of oxygen in the dialysed air was found as high as 41·96 per cent., it fell with the same septum to 38·65 per cent., with an aspiration of $0^{m}{\cdot}668$; 33·05 per cent. with an aspiration of $0^{m}{\cdot}570$; 27·65 per cent. with an aspiration of $0^{m}{\cdot}380$; 24·83 per cent. with an aspiration of $0^{m}{\cdot}190$. Such a result is indeed a necessary consequence of the theory of gases. Air under a pre s

6. *Percolation of Air through Gutta-percha and other Septa.*

Thin transparent sheets of a certain material represented as air- and water-tight are in common use. It is often spoken of as consisting of caoutchouc, but appears to have a body of gutta-percha, softened probably by a drying-oil. From its softness and thinness, this sheet of gutta-percha appeared at first highly promising. But it appears not to be free from small apertures for any considerable surface. When a small sound portion was operated upon, air was found to percolate through it very slowly. In a tube diffusiometer of 1·3 metre in length and 20 millims. in diameter, closed at the top with this septum supported by stucco, the mercurial column fell from 28·7 to 22·625 inches in 18½ hours. The gas which had entered above the mercury measured 13·54 cub. centims., and was found to contain 20·2 oxygen to 79·8 nitrogen—a proof that the air had entered by gas-diffusion. The material is in fact of sufficient porosity to permit the molecular passage of gases in a slow manner.

Varnishes of gelatin and of drying-oil have been tried as dialytic septa, but hitherto without marked results.

Part II.—Action of Metallic Septa at a Red Heat.

Platinum.

The surprising passage of gases through the homogeneous substance of a plate of fused platinum or of iron at a red heat, lately discovered by MM. H. Ste.-Claire Deville and Troost, may possibly prove to be analogous in its mode of occurrence to the passage of gases through the rubber septum. At the same time it must be admitted that such an hypothesis as that of liquefaction can only be applied in a general and somewhat vague manner to bodies so elastic and volatile at an elevated temperature as the gases generally must be, and hydrogen in particular. Still some degree of absorbing and liquefying power can scarcely be denied to a soft or liquid substance, in whatever

sure of two atmospheres was dialysed in escaping through a rubber septum without exhaustion; but the proportion of oxygen passing never exceeded 36·5 per cent. of the air, or was sensibly less than in the experiments with a vacuum.—April 3, 1867.

circumstances it may be found, with such a patent fact before us as the retention by fused silver of 18 or 20 volumes of oxygen at a red heat. It may safely be assumed that the tendency of gases to liquefaction, however much abated by temperature, is too essential a property of matter to be ever entirely obliterated.

A little consideration also shows that the absorption of gas by a liquid or by a colloid substance is not a purely physical effect. The absorption appears to require some relation in composition—as where both the gas and the liquid are hydrocarbons, and the affinity or attraction of solution can come into play. May a similar analogy be looked for, of hydrogen to liquid or colloid bodies of the metallic class?

With reference to the mechanical pores of a solid mass, liquids are probably more penetrating than gases. The former show often a power of adhesion to solids, while gases appear to be essentially repulsive. A degree of minute porosity is conceivable, which will admit a liquid, but may be impassable to a gas, even under its molecular movement of diffusion.

Finally, there is presented to us a bold and original conjecture by M. Deville, in explanation of his own observations. It is clearly expressed in the following quotation taken from the last publication of M. Deville on this subject:—

"La perméabilité de la matière est d'une nature toute différente dans les corps homogènes, comme le fer et le platine, et dans des pâtes plus ou moins discontinues, resserrées par la cuisson ou la pression, comme la terre à creuset, la plombagine, dont M. Graham s'est servi dans ses mémorables expériences. Dans les métaux, la porosité résulte de la dilatation que la chaleur fait éprouver aux espaces intermoléculaires; elle est en relation avec la forme des molécules que l'on peut toujours supposer régulières, et avec leur alignement qui détermine le clivage ou les plans de facile fracture des masses cristallisées. C'est cet intervalle intermoléculaire que le phénomène de la porosité des métaux purs et fondus accuse avec une évidence éclatante, c'est aussi par ce phénomène qu'on peut espérer de calculer la distance des molécules solides aux températures élevées où les gaz peuvent s'y introduire."

A new kind of porosity in metals is imagined, of a greater degree of minuteness than the porosity of graphite and earthenware. This is an intermolecular porosity due entirely to dila-

tation. The intermolecular porosity of platinum and iron is not sufficient to admit any passage of gas at low temperatures, but is supposed by M. Deville to be developed by the expansive agency of heat upon the metals, and to become sensible at the temperature of ignition. Such a species of porosity, if it exists, may well be expected to throw light on the distances of solid molecules at elevated temperatures, when gases introduce themselves. The ready passage through platinum of some gases, particularly of hydrogen, and the difficult passage of others render such molecular views the more remarkable.

The passage of hydrogen through the substance of heated platinum appears in its most simple aspect when the gas is allowed to make its way through the metal into a vacuous space. The experiment of M. Deville, where a tube of platinum charged with nitrogen is placed within a large porcelain tube charged with hydrogen,* was modified by placing the platinum tube, closed at one end, in communication by the other (open) extremity with the Sprengel pump, so that a vacuum was substituted for the nitrogen. It was then easy to observe that a vacuum in the platinum tube was preserved for hours when the external gas admitted into the annular space between the porcelain and platinum tubes was either atmospheric air or hydrogen at the natural temperature. The tubes being placed across an empty furnace, the latter was now lighted; and it was seen that, with air circulating outside the platinum, the vacuum remained undisturbed, even when the temperature of the tubes rose to a bright red heat. But when dry hydrogen was driven through the same annular space, the platinum, while continuing impermeable at all temperatures below a dull red heat, began to admit hydrogen to the vacuum as soon as the external porcelain tube became visibly red-hot. In seven minutes the Sprengel pump now delivered 15·47 cub. centims. of gas, of which 15·27 cub. centims. appeared, by explosion with oxygen, to be hydrogen.

In a repetition of the last experiment, hydrogen dried by sulphuric acid was again allowed to circulate in excess outside the platinum. After a vacuum was once obtained within the platinum tube, the gas delivered by the Sprengel pump, in the cold, during a period of forty minutes, amounted to no more than a bubble of the size of a pin-head, showing the tightness of

* Comptes rendus, vol. lvii, p. 965.

the apparatus. The Sprengel pump being constantly kept in action, the tubes were now heated to redness, and then gradually to a temperature approaching a white heat. The gas delivered each five minutes was found to be 13, 15·5, 17·4, 16·9 18·6 cub. centims. as the temperature rose. These volumes are referred to a temperature of 20°, and barometer of 760 millims. The last observation gives a passage of 3·72 cub. centims. of hydrogen per minute. The platinum tube employed here was joined without solder, having been drawn from a mass of platinum which had been aggregated by fusion. It was similar in this respect to the tube employed by M. Deville. The tube was 0·812 metre in length (32 inches) and 1·1 millim. in thickness, with an internal diameter of 12 millims. But only a portion of about 200 millims. (8 inches) of the tube were heated to redness in the furnace experiment. The inner surface of the heated portion has therefore an area of 0·0076 square metre. Hence one square metre of heated platinum delivers 489·2 cub. centims. of hydrogen per minute. This result admits of comparison with the passage of gases through a septum of rubber. In the most favourable circumstances, when the thin membrane of a rubber balloon was employed, the passage of air into a vacuum was at the rate of 26·5 cub. centims. per square metre in one minute. The passage of hydrogen may be taken as 4·8 times as rapid as that of atmospheric air, or at 127·2 cub. centims. per minute. But while the thickness of the platinum septum was 1·1 millim., that of the rubber film was only one-seventieth part of a millimetre. Hence we have the ultimate comparison :—

Passage of hydrogen gas in one minute through a septum of 1 square metre;

Through rubber 0·014 millim. in thickness, 127·2 cub. centims. at 20° C.;

Through platinum 1·1 millim. in thickness, 489·2 cub. centims. at bright red heat.

If the permeation of hydrogen is due to the same agency in both septa, can the vast superiority of the platinum septum be connected with its greatly higher temperature?

It was interesting now to turn from hydrogen to the passage of other gases through heated platinum. The experiments were all made in the same way, and at a full red heat. The temperature, it will be observed, was short of that at which the

elements of water and carbonic acid are partially dissociated.

Oxygen and Nitrogen.—Atmospheric air, which may be taken to represent both of these gases, was now allowed to flow through the annular space between the tubes, the interior platinum tube being kept vacuous as usual. In one hour the gas collected by the constant action of a Sprengel pump amounted only to 0·3 cub. centim. Hydrogen in the same time would have given 211 cub. centims. It is very doubtful, too, whether the trifling fraction of a centimetre of gas collected had all passed through the platinum; a part (or the whole of it) may have entered by the joints of the apparatus. Platinum, then, cannot be said to be sensibly permeable to either oxygen or nitrogen, even at a full red heat.

Carbonic Acid.—This gas was supplied from a bottle containing marble, by the action of pure hydrochloric acid, the gas being afterwards washed with water and dried by sulphuric acid in its way to the exterior porcelain tube. In one hour the interior platinum tube yielded only three-tenths of a cubic centimetre of gas, of which, again, only an indeterminate small portion was condensed by baryta water and appeared to be carbonic acid. The passage of carbonic acid is therefore incalculably small at a full red heat.

Chlorine.—This gas, evolved slowly from a glass flask containing peroxide of manganese and hydrochloric acid, was washed by water, dried by sulphuric acid, and thrown as usual into the porcelain tube so as to occupy the annular space between the two tubes. A small tube containing slaked lime was interposed between the end of the platinum tube and the Sprengel pump, so as to absorb the chlorine, if any came through the substance of the platinum. After the tube had been heated for an hour, the lime was examined for chlorine, but did not contain a trace of that substance. A minute quantity of gas, probably air, amounting to 0·15 cub. centim., was collected during the time. Platinum, then, is not sensibly penetrated by chlorine at a red heat.

Hydrochloric acid, dried over sulphuric acid, was passed for one hour through the porcelain tube. About 0·5 cub. centim. of gas was collected from the platinum tube, which contained no hydrochloric acid and no free hydrogen. The ignited platinum, then, is not penetrated by hydrochloric acid; nor does it appear to

dissociate the elements of that gas at the temperature of the experiment.

Vapour of Water.—A stream of steam was carried for one hour through the porcelain tube. During that time half a cub. centim. of gas appeared to be drawn from the platinum tube, which gas contained no hydrogen. There is no evidence of the passage through the platinum of the vapour of water, nor of its decomposition.

Ammonia.—This gas appeared to be decomposed to a considerable extent in passing through the heated annular space, hydrogen passing freely at the same time through the ignited platinum. No trace of undecomposed ammonia, although the gas was transmitted in considerable excess, was discovered accompanying the free hydrogen found in the platinum tube. When the ammonia was evolved slowly, the quantity of hydrogen entering the platinum tube amounted to 16·4 cub. centims. in five minutes, or was sensibly the same as when pure hydrogen was carried through the annular space. Ammonia, then, appears to be incapable of penetrating the ignited platinum.

Coal-gas.—When coal-gas was carried through the porcelain tube, the following quantities of hydrogen came through the platinum in successive periods of twenty minutes each, 13·3 cub. centims., 5·2, and 8·8. The first portion, when exploded with oxygen, did not disturb baryta-water after condensation; 13·3 cub. centims. contained 13·16 cub. centims. of hydrogen. It appears, then, that the permeating gas was free hydrogen only, and that no compound of carbon present in coal-gas was capable of passing through the platinum. This may be held as excluding the passage of *carbonic oxide*, *marsh-gas*, and *olefiant gas*, all represented in the coal-gas.

Hydrosulphuric Acid.—This gas, prepared from sulphide of antimony and hydrochloric acid, washed, and dried over chloride of calcium, was then circulated through the outer porcelain tube. The hydrosulphuric acid was nearly all decomposed into sulphur and hydrogen, the latter coming through the platinum at the rate of 9 cub centims. in five minutes. A trace of hydrosulphuric acid may also have passed through, as the mercury of Sprengel's tube was slightly soiled; but no indication of this gas could be perceived in the hydrogen collected. It appears, then, that hydrosulphuric acid is to be classed

among the non-penetrating gases. The result appears to be:—

I. Gas capable of passing through a septum of platinum 1·1 millim. in thickness at a full red heat.

Hydrogen (211 cub. centims. per hour).

II. Gases incapable of passing through a septum of fused platinum 1·1 millim. in thickness at a full red heat.

Oxygen.....	(not to the extent of 0·2 cub. centim. per hour.)	
Nitrogen	,,	,,
Chlorine	,,	,,
Hydrochloric acid .	,,	,,
Vapour of water ..	,,	,,
Carbonic acid	,,	,,
Carbonic oxide....	,,	,,
Marsh-gas (CH_4) ..	,,	,,
Olefiant gas	,,	,,
Hydrosulphuric acid	,,	,,
Ammonia	,,	,,

It remains to be discovered whether a sensible passage of any of these gases could be effected through a platinum septum much reduced in thickness, or through the same septum under the influence of a considerably higher temperature. A fallacious appearance of permeation is sometimes occasioned by the escape from the platinum itself of a small quantity of gas, particularly of carbonic oxide and hydrogen, as will immediately appear. The permeation is in consequence never unequivocal for the first hour or two that the platinum septum is heated.

One of the curious experiments of M. Deville was repeated, in which hydrogen appears to escape from the platinum tube pretty much as the same gas would escape from a graphite diffusiometer—the platinum tube being full of hydrogen, while the annular space between the platinum and outer porcelain tube was occupied by atmospheric air. At the maximum temperature the supply of hydrogen to the platinum tube was shut off, as that gas entered at one end of the tube, while the other end of the platinum tube was left in connexion with a barometer-tube dipping into a cistern of mercury. Immediately the mercury began to rise in the gauge-tube from the passage of

hydrogen outwards through the walls of the platinum tube; and the latter in the end became nearly vacuous from the complete escape of the hydrogen.

Heated platinum tube containing hydrogen; air outside.

Time.	Rise of mercury in gauge barometer.
0 minute.	0 millim.
10 minutes.	115 millims.
20 „	245 „
30 „	400 „
40 „	535 „
50 „	645 „
60 „	710 „

the actual height of the atmospheric barometer being 750 millims. at the same time. The tension of the residual gas was therefore no more than 40 millims. of mercury. The ratio between the volume of gas at the beginning and end of the hour is here as 18·75 to 1; whereas in a diffusion experiment of hydrogen into air, the ratio would be as 3·8 to 1. Further, the residual gas in the platinum tube still retained a small portion of hydrogen. Withdrawn by means of the Sprengel pump and examined, the residual gas in the platinum tube amounted to 3·56 cub. centims., and consisted of

Nitrogen	3·22 cub. centims.
Hydrogen.....	0·34 „
	3·56

The available capacity of the platinum tube was 113·1 cub. centims.; and when the tube was heated, the gas driven out by dilatation measured in the cold 39·5 cub. centims., leaving in the hot platinum tube 73·6 cub. centims. of gas estimated at 20° C., and barom. 760 millims. It was found necessary in these experiments to stuff that portion of the platinum tube that was placed across the furnace and strongly heated, with asbestos, to give support to the tube when softened by the heat of ignition, and to prevent the tube from collapsing.

It is difficult to say where the small volume of nitrogen found in the platinum tube, amounting to 3·22 cub. centims., actually came from. It appears too great in amount to have formed an

impurity in the original hydrogen gas, or to have gained access to the vacuum through defective joinings in the apparatus. Its presence suggests the inquiry, admitting that nitrogen cannot pass alone through platinum into a vacuum, whether the same gas may not be enabled to pass, in some small proportion, while hydrogen is simultaneously travelling through the platinum in the opposite direction. The liquid or the gaseous hydrogen occupying the platinum septum would thus form a vehicle or channel, by the help of which another analogous body like nitrogen might be conceived capable of passing through the platinum in small quantity, by a process of liquid or gaseous diffusion.

Absorption and detention of Hydrogen by Platinum.—The passage of a gas through a colloid septum is preceded by the condensation of the gas in the substance of the septum, according to the views taken in this paper. Is a plate of ignited platinum capable, then, of condensing and liquefying hydrogen gas? The subject could scarcely admit of experimental investigation without the application of the same useful air-exhauster that was employed with the non-metallic colloids. The metal was always treated in the same manner; so that a description of the details of one experiment will apply to all.*

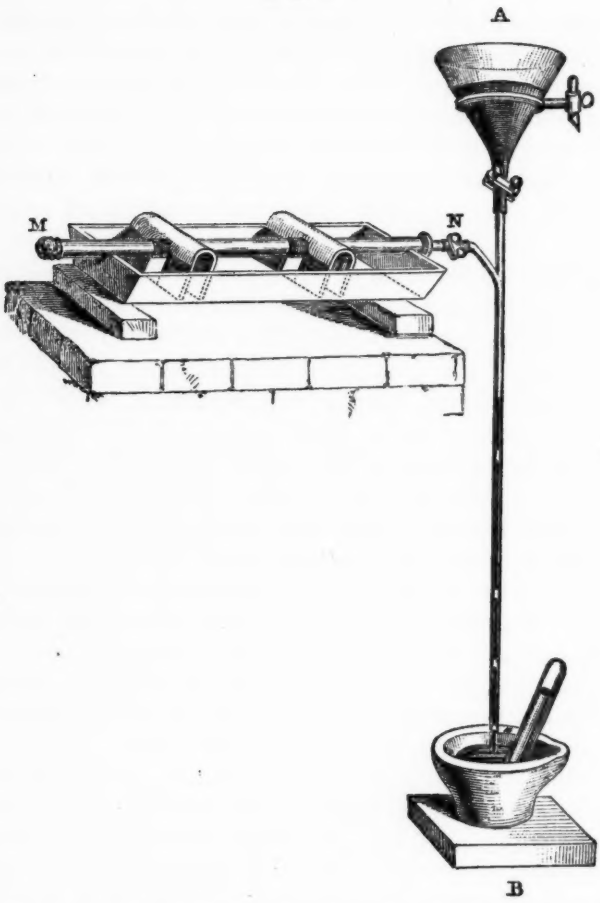
Platinum wire or plate being provided, the surface of the metal was first divested of all adhering oily matter, by boiling in caustic alkali and afterwards in distilled water.

The platinum, generally in the form of wire, was then introduced into a porcelain tube M, N (fig. 2), glazed both outside and inside, 0·55 metre in length and 23 millims. in internal diameter. This tube could be heated either by means of the combustion-furnace used for organic analysis, or by placing the tube across the chamber of a small cylindrical furnace. The porcelain tube was fitted at both ends with perforated corks, well cemented with fused gutta-percha, and provided each with a small quill tube. Such may be described as the distillatory apparatus employed. It was connected at the end N with the Sprengel pump A B, to be used as an exhauster and transferrer of gas, by means of good caoutchouc adapters (not vulcanized) and at the other end, M, with the apparatus for supplying dry

* Platinum in the peculiar condition of platinum-black absorbs 745 times its volume of hydrogen gas.—Traité de Chimie Généralé, par MM. Pelouze et Frémy, t. iii, p. 398.

hydrogen, atmospheric air, or any other gas. By means of a cork, or by a screw clamp upon the adapter at M, the tube could be

Fig. 2.



closed, and the gas-producing apparatus then detached, leaving the porcelain tube shut at one end. A tube of the hard glass used in combustion analysis, may be substituted for the porcelain tube in many such experiments. A less degree of heat suffices than was at first supposed.

The porcelain tube is exhausted by continuing the action of the Sprengel for ten or fifteen minutes, till small bubbles of gas cease to be delivered by the tube A B in the mercurial trough

below. The sufficiency of the joints is thus first ascertained. Heat being then applied to the porcelain tube, its impermeability at a red heat will also be tested.

The masses of platinum, when introduced, were confined to about two-thirds of the central portion of the porcelain tube, which could be conveniently heated. The apparatus obviously affords the means both of heating the platinum in a vacuum and also in an atmosphere of hydrogen or any other gas admitted into the interior of the porcelain tube at M.

Fused Platinum.—Articles of manufactured platinum appear now to be prepared exclusively from the fused metal.

1. A quantity of clean platinum wire from fused metal, measuring 0·695 metre in length, 4·1 millims. in diameter and 201 grms. in weight, was bent and introduced into the porcelain tube, which was then exhausted. The platinum was first heated alone for an hour to drive off any natural gaseous product, and then dry hydrogen gas was admitted to the porcelain tube, the gas being evolved from pure sulphuric acid and pure zinc. The hydrogen was conveyed in excess into the porcelain tube, at a cherry-red heat, and the temperature was then allowed to fall in a gradual manner—a procedure which was found to promote the absorption of the gas. The platinum was thus retained for about twenty minutes in an atmosphere of hydrogen, at a temperature partly above and partly below dull redness, terminating with the lower temperature. After the fire was withdrawn and the tube allowed to cool, air or nitrogen was driven through it, and all free hydrogen thus expelled from the apparatus.

The closed tube was now exhausted in the cold, but no hydrogen came off. The platinum being still retained in a good vacuum, heat was again very gradually applied, and the action of the Sprengel pump maintained. Simultaneously with the first appearance of visible ignition, gas began to be evolved. In one hour, the porcelain tube being heated to redness, 2·12 cub. centims. of gas were collected, of which about one-third was collected in the first ten minutes. It was found, by explosion with oxygen, to consist of—

Hydrogen.....	1·93 cub. centim.
Nitrogen	0·19 „

Now, taking the specific gravity of the platinum wire at 21·5,

the volume of 201 grms. of metal will be 9·34 cub. centims. Hence one volume of platinum held, the gas being measured cold,

0·207 vol. hydrogen.

The platinum did not appear sensibly altered in lustre, or in any other way, by its relation to the hydrogen.

2. The same piece of platinum wire was drawn out into four times its first length, and the experiment of charging with hydrogen was repeated. The platinum gave up at a red heat, maintained for one hour, 1·8 cub. centim. of gas, of which 1·6 cub. centim. was hydrogen. Here one volume of platinum appears to have held

0·171 vol. hydrogen.

The absorption of hydrogen has not been increased by increasing the surface of the metal.

In two further experiments upon the same platinum wire, the volume of hydrogen retained by one volume of platinum was—

3. 0·173 cub. centim. hydrogen.

4. 0·128 „ „

There is an evident tendency of the hydrogen taken up to diminish in quantity. These experiments have the advantage for comparison with the earlier observations on the penetration of a platinum septum by hydrogen gas, that both wire and tube had been drawn out from the same mass of fused metal. No iridium had been added to this platinum, as is sometimes done to increase the elasticity of the metal. The absorption of hydrogen is small, amounting, according to the mean of the four observations, to 17 per cent. of the volume of the platinum. At the temperature of a low red heat, when the absorption took place, the gas would be considerably dilated, to the extent of at least three times its volume stated above, or to about 51 per cent., half the volume of the platinum. It is to be considered whether an absorption of half a volume of gas would be sufficient to account for the observed penetration of a septum of metal 1·1 millim. in thickness. The data appear to favour an affirmative conclusion; but their value cannot be very decidedly estimated.

It appears necessary to recognize in platinum a new property, a power to absorb hydrogen at a red heat, and to retain that gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power to occlude (to

shut up) hydrogen, and the result as the *occlusion* of hydrogen by platinum.

The observation was extended to platinum in other conditions of form, but where, it is to be observed, the metal had not been fused, but only welded, and was not of recent manufacture.

5. Of the grey pulverent spongy platinum, prepared from the ammonio-chloride, 22·2 grms. were heated by the combustion-furnace, and for half an hour allowed to cool gradually in dry hydrogen gas, as in the preceding experiments. The volume of the platinum is 1·032 cub. centim. by calculation. In the first experiment it yielded to heat and the action of the Sprengel pump 2·2 cub. centims. of gas which burned like hydrogen. In a second experiment the platinum yielded in one hour (when it appeared to be exhausted) 1·7 cub. centim. of gas, found by explosion to consist of hydrogen 1·52 cub. centim., and nitrogen 0·18 cub. centim. Here one volume of spongy platinum appears capable of occluding

1·48 vol. hydrogen.

6. Wrought platinum, in the form of plate from an old crucible cut up, after washing and ignition, was charged with hydrogen three times in succession. The weight of the platinum was 24·1 grms., and its volume 1·12 cub. centim. It yielded in seventy-five minutes 4·19 cub. centims. of gas, and in thirty minutes further 1·5 cub. centim. more, making together 5·69 cub. centims., of which 4·94 cub. centims. proved to be hydrogen; therm. 14°·2, barom. 760 millims. Not a trace of carbonic acid was found in the gas before or after explosion. Again, after a second charge, 5·12 cub. centims. of gas were given up in an hour, of which 4·4 were hydrogen; and lastly, 3·76 cub. centims. in an hour, of which 3·42 were hydrogen. Hence occluded by 1 vol. wrought platinum—

5·53 vols. hydrogen.
4·93 „ „
3·18 „ „

The volume of occluded hydrogen is much larger than in the fused platinum, or even in the spongy platinum. It exhibits a tendency to fall off on repeating the experiment. But the declension in absorbing-power may be connected with the reduced duration of the exposure to hydrogen of the metal while cooling, both in the present and former experiments.

7. Wrought platinum, which had been formed many years ago into a small tube, weighing 64·8 grms., 0·322 metre in length, and 5 millims. in diameter, was cut into three equal lengths for convenience in placing the metal within the porcelain tube, to be heated and charged with dry hydrogen. By an hour's exhaustion afterwards the platinum yielded 9·2 cub. centims. gas, of which 8·9 were hydrogen. The volume of the platinum itself was 3·9 cub. centims.; and one volume of metal had therefore occluded 2·28 vols. hydrogen, measured at about 20° C. In all such experiments, besides blowing out the free hydrogen by air, the apparatus was also thoroughly exhausted by the Sprengel pump in the cold, before the occluded hydrogen was extracted.

The lustre and appearance of the metallic platinum was not altered by the ingress of the hydrogen; but after the escape of the gas the platinum appeared whiter in colour, and the surface to be covered by minute blisters.

Repeating the experiment, the gas collected by an hour's exhaustion was 8·7 cub. centims., of which 8·46 cub. centims. were hydrogen. Here the metal occluded 2·8 vols. of hydrogen.

The same platinum was a third time charged with hydrogen; but on this occasion the platinum was placed in a tube of hard glass, and the tube connected with the air-exhauster. The glass tube was heated by an oil-bath, and the platinum kept *in vacuo* at a temperature of 220° C. for an hour. Not a bubble of gas was evolved. The glass tube was afterwards heated by a small Bunsen burner, which was calculated to give a degree of heat little short of visible redness, still no hydrogen came off. The tube was now heated sufficiently to soften glass (500°). Gas began to come off, of which 1·8 cub. centim., containing 1·72 hydrogen, were collected in ten minutes. The glass tube having cracked, the whole apparatus was allowed to cool, and the platinum transferred to a porcelain tube. Further heated by a combustion-furnace for one hour, the platinum gave off 8·6 cub. centims. gas, of which 8·2 were hydrogen. The platinum therefore appears to have occluded altogether 3·79 vols. of hydrogen.

The preceding experiment appeared to show a complete sealing up of the occluded hydrogen at low temperatures, seeing that, although nearly four volumes of gas were present, none escaped below a red heat. But to test the effect of time at the

temperature of the atmosphere, the platinum, again charged with hydrogen, was sealed up hermetically in a glass tube, which it nearly filled, and not opened for two months. The air in the tube was then transferred and examined. It did not exhibit any reduction of volume under the electric spark or a pellet of spongy platinum. The air therefore appeared to contain no hydrogen; the latter had not diffused out, but, it is to be presumed, was retained by the platinum without loss. These experiments, although related last, were the first performed in this enquiry. The included hydrogen was never entirely extracted in an hour, and is probably understated. The gas always came off gradually, more than one-half of the whole in the first twenty or thirty minutes. The last results may be stated as follows:—

1 vol. hammered platinum occluded 2·28 vols. hydrogen.
" " " 2·80 "
" " " 3·79 "

The high absorbing power of the hammered platinum, or rather the low absorbing power of the fused metal, was ascribed to a mechanical difference between the two—to a more open texture in the former, permitting more free access of hydrogen, liquefied as it may be, to the interior of the metal.

8. The extrication of occluded hydrogen from platinum had always required a degree of temperature verging upon a red heat, even when aided by a vacuum; and this remains true of hydrogen originally absorbed at or near a red heat. But the fact appears to be compatible with the absorption of the gas, under the pressure of the atmosphere, at a considerably lower temperature. Thin platinum-foil was first deprived of a little natural gas by ignition *in vacuo* in the porcelain tube. The foil was afterwards placed in a glass tube and heated again in a stream of hydrogen, to a temperature not exceeding 230° C., for three hours, by means of an oil-bath, and further allowed to cool slowly in an atmosphere of the same gas for several hours. A second glass tube receiver, to which the platinum-foil was transferred, was exhausted, as usual, at 20° C. without any sensible evolution of gas. With a red heat superadded, gas came off in twenty minutes (but nearly all in the first seven minutes) to the extent of 0·75 cub. centim., of which 0·56 cub. centim. proved to be hydrogen. The volume of 8·3 grms. of

platinum is 0·385 cub. centim. Hence one volume of platinum foil appears to take up, in three hours,

1·45 vol. hydrogen at 230° C.

9. The same portion of platinum foil was again charged with hydrogen at a still lower temperature, namely between 97° and 100°, for three hours. Submitted to exhaustion at red heat, the platinum now gave off 0·5 cub. centim. of gas in thirty-five minutes, of which about 0·3 cub. centim. was hydrogen. One volume of platinum-foil has taken up

0·76 vol. hydrogen at 100°.

By this property platinum is connected with palladium, which of all metals appears to possess the power of absorbing hydrogen in the highest degree.

Palladium.

Of late years palladium has become comparatively uncommon; and some difficulty was experienced at first in procuring more than a gramme or two of the metal, in the form of thin foil. The palladium-foil first employed weighed 1·58 grm., and measured 0·133 cub. centim., taking the specific gravity of the metal at 11·86, and had a surface of 0·00902 square metre. It gave off, when heated *in vacuo* for one hour, 1·50 cub. centim. of natural gas, containing no compound of carbon, but consisting of hydrogen and air.

1. As it appeared from preliminary experiments that the occlusion of hydrogen by palladium was likely to be a phenomenon exhibited at a comparatively low range of temperature, the metal was heated in hydrogen no higher than 245° C., by an oil-bath, and allowed to cool very slowly, so as to pass through still lower ranges of temperature which might be favourable to the absorption of hydrogen. The metal, when afterwards transferred to a distillatory glass tube, appeared to give out nothing to a vacuum at 17°·8 C. and barom. 759 millims. But the moment the combustion-furnace was lighted under the tube, gas came off most freely. Of the first portion collected, 11·77 cub. centims. contained 11·74 cub. centims. hydrogen. The gas ceased to be evolved in fifteen minutes, when 69·92 cub. centims. were collected, of which the greater part came over in the first

ten minutes. Hence palladium has taken up a large volume of gas when the temperature of the metal never exceeded 245° C.

1 vol. palladium held 526 vols. hydrogen.

2. In a similar experiment the temperature of absorption was still further lowered with good effect. The palladium was exposed to hydrogen between 90° and 97° C. for three hours, and then allowed to cool in the gas for one hour and a half. Now placed in a glass tube, exhausted, and heated by a gas-flame, the palladium gave off gas in a continuous stream for twelve minutes, when it ceased. The gas amounted to 85·56 cub. centims., of which 96·8 per cent. was hydrogen; therm. 17°·5, barom. 764 millims.

1 vol. palladium held 643·3 vols. hydrogen.

By the care of my zealous assistant, Mr. W. C. Roberts, the hydrogen employed in these experiments was purified to the highest degree by passing it in succession through alcohol, water, caustic potash, and tubes of 0·7 metre each, filled with broken glass impregnated with nitrate of lead, sulphate of silver, and oil of vitriol. The gas was inodorous, and burned with a barely visible flame.

No alteration was sensible in the metallic appearance of the palladium-foil when charged with hydrogen, or when discharged. The foil was much crumpled, and rather friable after repeated use; but this may have arisen from frequent handling.

3. Palladium appears to absorb hydrogen largely, even at natural temperatures, provided that the metal has been recently ignited *in vacuo*. The foil, without such preparation, was placed in a bottle of pure hydrogen for several hours, but yielded nothing when afterwards ignited in the Sprengel vacuum. The foil, however, being immediately returned after cooling to a stoppered bottle containing hydrogen, and left in the gas for a night, absorption now took place—air rushing in, on opening the stopper, as into a partial vacuum; therm. 19°. When the palladium-foil was afterwards transferred to a glass-tube and connected with the Sprengel pump, it was found difficult to obtain a vacuum for some time, owing to hydrogen coming off at the temperature of the atmosphere. But after a fair vacuum was produced, 6·96 cub. centims. were collected, of which 6·78 proved to be hydrogen. Heat was then applied, and 42 cub.

centims. came over in five minutes, making altogether more than 50 cub. centims., or 376 volumes of gas. The absorption of hydrogen appears, then, to be suspended at a low temperature, unless the condition of the metal be favourable. The action of a plate of clean platinum in determining the combustion of explosive gas is equally critical at a low temperature.

4. A different specimen of palladium-foil, weighing 5·76 grms., and having a volume of 0·485 cub. centim., was charged with hydrogen, and discharged, more than once. In the second experiment, the foil was heated in hydrogen at 100° for three hours. Distilled afterwards in a porcelain tube at a low red heat in the usual way, the palladium was found to have absorbed, at 100°,

347·7 vols. of hydrogen measured at 18°·2 C. and barom. 756 millims.

5. So large an absorption of hydrogen should increase the weight of the palladium sensibly, notwithstanding the lightness of the gas. One litre, or 1,000 cub. centims., of hydrogen at 0° C. and 760 millims. weighs 0·0896 grm. Of new palladium-foil, believed to be from *fused* metal, 5·9516 grms. increased to 5·9542, or by 0·0026 grm., when the metal was charged with hydrogen at 100° for four hours. This amounts to only 29·01 cub. centims. of hydrogen at 0° C. and 760 millims. barom. The gas actually extracted afterwards from the palladium did not exceed 34·2 cub. centims. at 19° C., and barom. 758 millims., equivalent to 31·84 cub. centims. at 0° C. and 760 millims. barom. The whole gas extricated (68 vols.) seems unusually small, but it corresponds closely enough with the volume calculated from the increase of the palladium in weight. An inferior absorbing power for hydrogen appears to be connected in both platinum and palladium with the fusion of the metal.

6. A portion of similar palladium-foil, charged with hydrogen, was found to have its gas reduced from 20·7 to 16·2 cub. centims. after exposure to the air for forty-two hours. The liquid hydrogen, whether held by the substance or in the pores of the metal, appears therefore to evaporate slowly at the temperature of the atmosphere, therm. 19°, barom. 752 millims.

7. Spongy palladium, from the ignition of the cyanide, being heated in hydrogen at 200°, and allowed to cool slowly in the same gas for four hours, the metal was found to have taken up 686 vols. of hydrogen.

Treated in a similar manner with air, spongy palladium exhibited no absorbing-power for oxygen or nitrogen.

Hydrogen, condensed either in the palladium sponge or foil, was observed to have its chemical affinities enhanced. The palladium being placed in dilute solutions of the following substances for twenty-four hours in the dark at the ordinary temperature, the action of the hydrogen became manifest.

Persalt of iron became protosalt.

Ferricyanide of potassium became ferrocyanide.

Chlorine-water became hydrochloric acid.

Iodine-water became hydriodic acid.*

Apart from hydrogen, the palladium sponge exhibits a power of selection and absorption of alcohol in preference to water. 30 grms. of the sponge were left in contact with 9·5 cub. centims. of dilute alcohol of specific gravity 0·893, for fifty-one hours, sealed in a tube. The supernatant liquid now drawn off to the extent of 3·9 cub. centims. was of specific gravity 0·901, while the portion retained by the palladium was found when distilled to be of specific gravity 0·885, or it was sensibly concentrated. This chemical action of palladium sponge was more than once verified. Platinum sponge, on the other hand, exhibited no indication of a similar separating power; nor did the sponge of iron reduced by hydrogen from the oxide.

8. Connected, it may be, with this chemico-molecular action of palladium is the variable absorptive power for different liquids exhibited by palladium-foil. Immersed in various liquids for an hour, and afterwards dried by pressure for a few seconds between folds of blotting-paper, a quantity of palladium-foil represented by 1,000 was found to retain in its pores—

Of water	1·18	part.
Of alcohol (0·802)	5·5	parts.
Of ether	1·7	part.
Of acetone (0·794)	0·54	„
Of glycerine	4·5	parts.
Of benzol	3·5	„
Of oil of sweet almonds	18·1	„
Of castor-oil	10·2	„

* The power of platinum-black charged with hydrogen to communicate the latter element to organic compounds has lately been observed by M. P. de Wilde, following Dr. Debus.—Bulletin de la Société Chimique, Mars, 1866.

The superior penetrativeness of alcohol over water is well marked; capillary action appears to merge into a chemical affinity. Liquid hydrogen would also appear as highly absorbable by palladium-foil. It would appear also to be separable from other gases (or liquids), as alcohol is from water, by the palladium-pores.

Alloy of 5 *palladium and* 4 *silver.*—The power to absorb hydrogen appears to extend to this alloy of palladium. A plate of the alloy, about 180 millims. in length, 31 millims. in width, and weighing 74·3 grms., was bent, so as to be able to enter a wide porcelain tube that could be exhausted of air when required. The volume of palladium alloy was 6·21 cub. centims. The plate of metal being placed in the porcelain tube, had hydrogen gas passed over it at a low red heat for one hour, and then was allowed to cool slowly in the same gas. Taken out and examined, the metal was not visibly altered. For the extrication of gas the metal was distilled in the porcelain tube heated by jets of gas, and connected with the Sprengel pump, as usual. In seven minutes after the gas-furnace was lit, 24 cub. centims. of gas came off; in ten minutes more, 80·71 cub. centims.; and in seventy-five minutes more, 36·75 cub. centims., making altogether 141·46 cub. centims. Of this gas 127·74 cub. centims. proved to be hydrogen, the remainder being nitrogen, derived, no doubt, from the large imperfectly exhausted porcelain tube. The palladium alloy, in the form of a thick plate, appears therefore to have held

20·5 vols. hydrogen, measured at 18°·2 and barom. 756 millims.

This alloy of palladium becomes crystalline by heating, and appears to lose much of its absorbent power at the same time.

The conclusion, then, is that welded palladium, in the condition of thin foil, readily absorbs hydrogen, to the extent of upwards of 600 times the volume of the metal at a temperature under the boiling-point of water, upwards of 500 volumes at 245°, and less at higher temperatures, the metal being always surrounded by hydrogen under atmospheric pressure. Hydrogen is also largely absorbed, although less constantly, at ordinary temperatures. On the other hand, palladium already fully charged with hydrogen at or under 100°, and under the pressure of the atmosphere, begins to give out gas when exposed either to atmospheric air or to a vacuum at the original

temperature of absorption; and the gas is freely discharged at 200° C.

It is probable that hydrogen enters palladium in the physical condition of liquid, whether the phenomenon proves to be analogous to the imbibition of ether, chloroform, and such solvents by the colloid india-rubber, or whether a certain porosity of structure in the palladium is required. The porosity of the metal is supposed to be of that high degree which will admit liquid but not gaseous molecules. Now the numerous liquid compounds of carbon and hydrogen have all a nearly similar density, generally a little under that of water. There is no reason to suppose that the density of liquid hydrogen would differ greatly from the hydrocarbon class; but then the surprising lightness of hydrogen gas must cause liquid hydrogen to yield a volume of vapour disproportionately large when compared with the former class of substances, or, indeed, with any other substance whatever. The absorption of hydrogen by palladium will appear, then, less extravagantly great when viewed as the absorption of a highly volatile liquid capable of yielding an exceedingly light vapour, rather than that of a gas.

An excellent opportunity of observing the penetration by hydrogen of a compact plate of palladium, 1 millim. in thickness, was afforded by a tube of that metal constructed by Mr. Matthey. This tube was said to have been welded from palladium near the point of fusion of the metal. The length of the tube was 115 millims., its internal diameter 12 millims., thickness 1 millim., and external surface 0·0053 of a square metre. It was closed by thick plates of platinum soldered at both ends, one of the plates being perforated by a long small tube of platinum, by which the cavity of the palladium tube could be exhausted of air.

Now the closed palladium tube remained air-tight, when exhausted by the Sprengel tube, at the ordinary temperature, at 260°, and at a temperature verging on low redness, the gas without being atmospheric air. Hydrogen being then substituted as the external gas, the walls of the palladium tube still remained impermeable at a low temperature. No hydrogen gained the interior in three hours at 100°. But the temperature being gradually raised by means of an oil-bath to 240°, hydrogen then began to come through, and at a gradually increasing

rate to 265°. The hydrogen then entered steadily at the rate of 8·67 cub. centims. in five minutes. This gives a rate of 327 cub. centims. for a square metre of surface per minute. Heated to a temperature just short of redness, the passage of hydrogen was increased to 11·2 cub. centims. in five minutes, or 423 cub. centims. for a square metre per minute.

With coal-gas as the external atmosphere the penetration of the palladium began about the same temperature, and was continued at 270° at the rate of 57 cub. centims. for a square metre of surface per minute. The penetrating gas had no odour of coal-gas, contained no trace of carbon, and appeared to be absolutely pure hydrogen. The exact isolation of the latter gas by septa of both platinum and palladium appears most extraordinary.

A quantitative determination of the hydrogen in a gaseous mixture could probably be effected by means of the hollow cylinder of palladium.

Is the power to penetrate the metals in question confined to hydrogen? It has been lately concluded by Dr. C. Wetherill that the turgescence of the ammonium-amalgam depends entirely upon the retention of hydrogen gas-bubbles;* hydrogen, then, appears to exhibit an attraction of a peculiar kind for mercury. The ready liquefaction of the same gas by the platinum metals evinces also a powerful mutual attraction. The only other volatile body which has been observed to pass, like hydrogen, through a plate of palladium is common ether—and that at the atmospheric temperature, while a passage was denied to hydrogen at the same time. The palladium was in the form of foil. Although thin foil of this metal is generally visibly porous and allows air to pass through like a sieve, a tube diffusiometer, covered with a disk of the selected palladium foil, and standing over mercury, retained a volume of 40·5 millims. of air over a vertical column of 155 millims. of mercury for twenty-four hours without depression of the mercury. The air was dried by sticks of potash, but still it did not penetrate the palladium. Dry hydrogen was then conducted to the upper surface of the palladium disk, but still without any penetration by that gas after several hours. Cotton-wool moistened with ether was now placed upon the disk, when, after eight minutes, the confined air within the tube began to

* American Journal of Science, vol. xlii, No. 124.

expand; and in the course of an hour longer, the 40·5 volumes of confined air increased to 90·4 (thermometer 18°·5, barometer 758), when the expansion ceased. The increase of volume appeared to be due entirely to ether-vapour, absorbable by a pellet charged with sulphuric acid. Why hydrogen proved to be incapable of penetrating the palladium in such circumstances it is difficult to say. It can only be imagined that the palladium foil may have previously condensed on its surface a minute film of foreign matter, which rendered the palladium inactive to hydrogen but not to ether-vapour.

On the other hand, the penetrating power of hydrogen, here referred to the liquefaction of that gas, appears not to be solely confined to metallic septa. There is reason to suspect that in diffusing through a plate of graphite, hydrogen passes in a small proportion as a liquid, without any counter-diffusion of air. Hence the constant excess observed of the diffusive coefficient of hydrogen, which came out 3·876, 3·993, and 4·067*, instead of the theoretical number 3·8, corresponding to the density of the gas referred to air. Such phenomena of gaseous penetration suggest a progression in the degree of porosity of solid bodies. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals, (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion, as in artificial graphite, and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite.

Osmium-iridium.

A portion of small grains of osmium-iridium, amounting to 2·528 grms., was exposed to hydrogen through all descending temperatures from a red heat, as the preceding metals had been treated. The osmium-iridium was then heated again to redness in the Sprengel vacuum, to extricate any hydrogen that might have been absorbed. But a bubble or two of gas, too minute to be measured, passed over in fifteen minutes, at a red heat. Osmium-iridium, then, exhibits no absorbent power for hydrogen —a result which is consistent with the crystalline character of the substance.

* Philosophical Transactions, 1863, p. 404.

Copper.

The power to occlude gases appears not to be confined to palladium and platinum among the metals. The exact experiments of M. Dumas, by which the atomic weights of the leading elements were definitely settled, afford an indication of the absorption of hydrogen gas by spongy metallic copper reduced from the oxide, sufficient to affect the weight of the metal to the extent of about 3 parts in 100,000*.

1. With the view of applying the method of extracting gas followed in the treatment of the preceding metals, so much oxide of copper was reduced by hydrogen as was calculated to yield 50 grms. of metallic copper. The reduced metal was again heated to redness and slowly cooled in a stream of dry hydrogen. After free exposure to the air for a few minutes, the metal was now submitted, at a red heat, to the action of the Sprengel pump. It then gave off in one hour 3·35 cub. centims. of gas, measured cold, which appeared to be pure hydrogen (the explosion with oxygen indicated 3·4 hydrogen). Taking the specific gravity of copper at 8·85, 50 grms. of that metal would be 5·65 cub. centims. in volume, and the result is that 1 vol. reduced copper sponge occludes 0·6 vol. hydrogen. Hydrogen being about 12,000 times lighter than copper (at 15°), 1 part of gas by weight has been taken up by 20,000 parts of metal.

2. The same weight and volume of fine copper, in the form of wire, thoroughly cleaned, was exposed to hydrogen at a red heat, and then submitted to exhaustion for one hour. It gave 2·6 cub. centims. gas. of which 2 cub. centims. were hydrogen, and the remaining 0·6 principally carbonic oxide. It may be represented that 1 vol. wrought copper occludes 0·306 vol. hydrogen.

Where a metal, such as wrought copper, may contain small quantities of carbon and oxygen, an obvious cause will exist for the production and evolution of carbonic oxide under the influence of heat.

* Annales de Chimie et de Physique, 3 sér., t. viii, p. 205. The observations of M. Melsens show that 240 grms. of copper may fix about 0·007 grm. of hydrogen, most being fixed when the oxide of copper is reduced by hydrogen at a low temperature. In the subsequent oxidation of the copper, the gas does not come out suddenly but in a gradual manner.

Gold.

1. A quantity of gold was precipitated from the assay cornettes used below by means of oxalic acid. The gold weighed 93·3 grms., with a volume of 4·83 cub. centims., taking the specific gravity of the metal as 19·31. Exhausted at a red heat without any further treatment, the reduced gold yielded 3·4 cub. centims. of gas, which may therefore be supposed to be gas usually present in gold reduced in the manner described. This is 0·704 vol. of the gold. The occluded gas in precipitated gold gave to analysis, 0·05 c.c. oxygen, 1·50 carbonic acid, 1·85 carbonic oxide, &c. (= 3·40 c.c.).

2. Of the original cornettes of fine gold, from gold assays conducted several months before, 93·3 grms., having a volume of 4·83 cub. centims., were submitted without any further treatment to aspiration at a red heat. The gold gave up in the first half hour 9·45 cub. centims. of gas, and in the second half hour 0·8 cub. centim., making together 10·25 cub. centims. Hence 1 volume of the gold cornettes appears to hold 2·12 volumes of gas. This gas consisted of 6·70 c.c. carbonic oxide, 1·50 carbonic acid, 1·58 hydrogen, 0·44 nitrogen, and 0·03 loss (= 10·25).

The cornettes do not appear ever to assume again so much gas as they first acquired in the assay muffle. It follows that the weight of a gold cornette is increased about 2 parts in 10,000 by the weight of occluded gas. As the gold also retains 7 or 8 parts of silver in 10,000, it follows that the absolute quantity of gold in a cornette is less than the weight of the cornette as indicated by the balance, by 1 part in 1000. This does not disprove the accuracy of the usual gold assay, which is always made in comparison with gold of known composition as a check, and is therefore *relatively* true.

3. The same volume of gold cornettes, amounting to 4·83 cub. centims., heated again in carbonic oxide gas, gave up afterwards 1·6 c.c. of occluded gas, composed of 1·4 c.c. carbonic oxide and 0·2 carbonic acid.

4. The same mass of gold cornettes, heated in hydrogen gas, gave up afterwards in one hour 2·7 cub. centims. of gas, which appeared to consist of 2·34 c.c. hydrogen and 0·36 nitrogen.

The power of this metal to occlude hydrogen gas is very sensible. The metal here appears to hold 0·48 volume of hy-

drogen gas. The same gold, when dissolved and precipitated, was also found capable of holding 0·44 volume of hydrogen.

5. The same mass of cornettes, heated in carbonic acid gas, gave up afterwards in one hour 1·05 cub. centim. gas, in which baryta-water showed the presence of 0·78 cub. centim. carbonic acid.

The charged cornettes were always freely exposed to air for some time before occluded gas was extracted from them and measured, so as to allow the escape of any loosely attached gas.

6. The same cornettes were heated and cooled in a stream of dry air, in like manner as they had been treated with other gases. The occluded air given out in one hour amounted in two different experiments to 1·15 and 0·95 cub. centim. respectively. The gas of the second experiment gave

0·82	cub. centim.	nitrogen....	=	86·3
0·08	„ „	carbonic acid	=	8·4
0·05	„ „	oxygen	=	5·3
0·95				100·0

The whole occluded air amounts to 0·2 volume of the gold, and is principally *nitrogen*. The indifference of gold to oxygen is remarkable, and contrasts with the power of silver to occlude the same gas.

Silver.

1. Fine silver, in the form of wire, 2 millims. in diameter, with its surface duly purified, was first heated alone in the porcelain tube, and then exhausted of gas by the Sprengel tube in the usual way. The natural gas derived from this metal was small in quantity, and it appeared to come off almost entirely in one hour. The silver wire weighed 108·8 grms., and had a volume of 10·37 cub. centims., taking the specific gravity of pure silver as 10·49. The gas extracted amounted to 2·2 c.c. in the first 30 minutes and 0·8 c.c. in the second, making 3·0 c.c. in an hour.

The gas consisted of 2·4 c.c. carbonic acid and 0·6 carbonic oxide.

Silver wire therefore appeared to hold occluded 0·289 volume of gas, principally carbonic acid. There is reason, however, to suppose that the occluded gas may really be oxygen, and that

the latter was converted into carbonic acid at the temperature of extrication, by a trace of carbon existing in the fine silver.

2. The same quantity of silver wire was now charged with hydrogen, by being heated to redness and afterwards cooled slowly in that gas. The gas extricated amounted to 2·3 c.c. in 45 minutes and 0·2 c.c. in the following 15 minutes, making 2·5 c.c. in one hour.

The gas consisted of 2·2 cc. hydrogen and 0·3 nitrogen, &c.

The fine silver had therefore occluded 0·211 volume of hydrogen. The metal acquired a beautiful frosted appearance on the surface; and by repeated heating it became highly crystalline and brittle.

3. The same portion of silver was now charged with oxygen. The occluded gas given off amounted to 7·5 c.c. in the first 30 minutes, and 0·3 c.c. in the second, making 7·8 c.c. in one hour.

The gas consisted of 7·6 c.c. oxygen and 0·2 hydrogen, &c.

The silver therefore held occluded 0·745 volume of oxygen. This gas, like the hydrogen in platinum, was permanently fixed in the metal at all temperatures below an incipient red heat. It did not tarnish the bright metallic surface of the silver, or produce any appearance suggestive of the oxidation of a metal.

4. The same portion of silver, after being dissolved in acid, precipitated as chloride, and reduced again, was exposed to atmospheric air at a red heat, and afterwards exhausted. The gas given off amounted to 5·56 c.c. in the first 15 minutes, and 0·30 c.c. in the second, making 58·6 c.c. in 30 minutes.

Of this gas 5·56 cub. centims., or nearly the whole, proved to be oxygen gas; or the silver held occluded 0·545 volume of oxygen. This silver had been purified from the chloride and it contained no trace of copper.

When silver, of British standard (that is, containing 7·5 per cent. of copper), is exposed to air or oxygen at a low red heat, the silver becomes almost black on the surface from oxidation of the copper. Silver wire in this blackened state gave off several volumes of oxygen under the action of heat and a vacuum. Much of the superficial oxide disappeared at the same time. It appeared as if the operation tended to the reduction of the superficial oxide of copper, oxygen being liberated, and the copper absorbed by the mass of silver.

5. A specimen of silver reduced from the oxide, in the form of sponge, which was considered pure, but was not analyzed,

occluded 6·15, 8·05, and 7·47 volumes of oxygen, in successive experiments, without any visible tarnish of the surface. Can the attraction or affinity of silver for oxygen, which enables the pure metal to occlude that gas, be enhanced by the presence of a mere trace of some positive metal like copper?

6. The same specimen of fritted silver was found to occlude, in successive experiments,

0·907 vol. hydrogen.
0·938 „ „
0·486 „ carbonic acid.
0·545 „ „ „
0·156 „ carbonic oxide.

Hydrogen and carbonic acid, as well as oxygen, appear to be taken up in larger proportion by this silver than by the former specimen of the same metal.

7. Of pure silver highly laminated, 500 leaves, weighing 12·5 grms., were exposed to air at a red heat, and thereafter exhausted at the same temperature. The silver (1 vol.) gave up 1·37 volume of oxygen, 0·20 volume of nitrogen, and 0·04 volume of carbonic acid.

It appears that silver has a relation to oxygen similar to that exhibited by platinum, palladium, and iron to hydrogen. The power of silver and of litharge in a state of fusion to absorb oxygen, and to allow that gas to escape on solidification, may be connected with the observed capacity of the colloid metal, softened by heat, to absorb the same gas, although to a less extent.

Iron.

The penetration of iron by hydrogen is demonstrated as clearly by MM. Delville and Troost as that of platinum. A thin tube of cast steel, 3 or 4 millims. in thickness, already enclosing hydrogen gas in its cavity, was surrounded by air or by nitrogen gas circulating in an annular space between the steel tube mentioned and a wider external porcelain tube. In the absence of any visible pores in the steel, hydrogen made its way through the substance of the metal, and escaped into the annular space as soon as the system of tubes was exposed to a red heat. A nearly if not entirely complete vacuum was formed

within the steel tube*. In another modification of the experiment, carbonic oxide from an uncertain source appeared within the steel tube, particularly when the temperature was most elevated†.

Wrought iron, in the form of thin wire (No. 23), about 0·4 millim. in diameter, first carefully cleaned with caustic alkali and water, was heated alone in the porcelain tube exhausted of air, for the purpose of eliminating any natural gases.

1. Of the iron wire referred to, 46 grms., with a volume of 5·9 cub. centims., the specific gravity of the metal being taken at 7·8, were heated by the open combustion-furnace. Gas came off freely at a red heat,—

(1) In fifteen minutes, 15·6 cub. centims., containing 3·5 cub. centims. carbonic acid, or 22·4 per cent. of the whole.

(2). In fifteen minutes, 7·17 cub. centims., containing 0·52 cub. centim., or 7·2 per cent. of carbonic acid. The gas of this and the following stages of observation now burnt with a blue flame, and was principally carbonic oxide.

(3.) In thirty minutes, 10·4 cub. centims., of which 6·86 cub. centims. were carbonic oxide.

(4.) In thirty minutes, 8·16 cub. centims., of which 0·12, or 1·4 per cent., was carbonic acid.

(5.) In thirty minutes, 5·52 cub. centims., of which 0·03 was carbonic acid—that is, 0·5 per cent.

Hence 46 grms. of wrought iron have in two hours given off 46·85 cub. centims. of gas, measured at about 15° C.; or 1 volume of iron has discharged 7·94 volumes of gas, of which about two-thirds was carbonic oxide; and the metal does not appear to be yet quite exhausted. Iron is a metal not unlikely to contain small quantities of carbon and oxygen, both in chemical union with iron; and the gas extricated may partly be due to a reaction of these elements upon each other at a red heat.

2. In another similar experiment upon 32 grms. of clean iron wire (No. 21), measuring 4·1 cub. centims., the iron was heated in a small glass tube, to exclude the idea of the conceivable permeability of the porcelain tube. The iron gave off gas at a pretty uniform rate, which amounted in an hour to 29·8 cub. centims., of which 4·44 cub. centims. were carbonic acid, and the remainder principally carbonic oxide, with hydrogen and a trace

* Comptes rendus, t. lvii, p. 965 (1863). † Ib. t. lix. p. 102 (1864).

of a hydro-carburet. Here the iron wire gave off 7·27 volumes of gas.

3. In a third experiment on thin iron wire (No. 23), the extrication of the natural gases at a red heat was pushed to a greater degree of exhaustion. The weight of the iron was 39 grms., and its volume 5 cub. centims. In the first and second hours, the gas collected was 45 cub. centims.; in the third hour 10·85 cub. centims.; in the fourth and fifth hours 5·65 cub. centims.; in the sixth hour 0·9 cub. centim., and in the seventh hour 0·7 cub. centim. The iron appears to be now nearly exhausted, after the extrication of 63·1 cub. centims., or 12·55 volumes of gas.

It is evident that iron cannot be safely dealt with in experiments upon the permeation or upon the absorption of gases, till these gases, whether self-produced or pre-existing, are first extricated from the metal. The carbonic oxide observed in the tube experiments of M. Deville may have been derived from the same source.*

4. To observe the absorption of hydrogen, the mass of exhausted iron wire remaining after the last experiment was heated to redness, and cooled gradually in the same gas. The metal was afterwards freely exposed to air (as usual) to get rid of any loosely attached hydrogen. Now exhausted again by the Sprengel pump at a low red heat, the iron gave 2·5 cub. centims. of gas in one hour, but the greater portion in the first ten minutes, consisting of

2·3	cub. centims.	hydrogen.
0·2	„ centim.	carbonic oxide, &c.
2·5		

The iron appears therefore to be capable of holding 0·46 volume of hydrogen. The wire became white, like galvanized iron. This was confirmed in a second observation, a thicker wire holding 0·42 vol. hydrogen.

5. The same specimen of iron was now charged with carbonic oxide gas, in the manner it had previously been charged with hydrogen. It was also freely exposed to air. The iron wire

* The gases which escape from cast-iron in a state of fusion have been examined by M. L. Cailletet. They appear to contain from 49 to 58 per cent. of carbonic oxide, 34 to 39 of hydrogen, and 8 to 12 of nitrogen.—Comptes rendus, t. lxi, p. 850 (1865).

remained soft, was not capable of becoming hard when heated red-hot and suddenly cooled, and was not altered in aspect or in solubility in acids. The gas extricated by the air-exhauster amounted to

9·45	cub. centims.	in	13	minutes.
2·43	„	„	5	„
8·05	„	„	42	„
3·15	„	„	60	„
23·08	„	„	in two hours.	

Of this gas 20·76 cub. centims. proved to be carbonic oxide. *Pure iron, then, is capable of taking up at a low red heat, and holding when cold,* 4·15 *volumes of carbonic oxide gas.* This fact was confirmed in various other experiments. It explains partly, if not entirely, the abundance of carbonic oxide observed among the natural gases of iron in experiments 1, 2, and 3. In the course of its preparation wrought iron may be supposed to occlude six or eight times its volume of carbonic oxide gas, which is carried about ever after. How the qualities of iron are affected by the presence of such a substance, no way metallic in its characters, locked up in so strange a way, but capable of reappearing, under the influence of heat, at any time, with the elastic tension of a gas, is a subject which metallurgists may find worthy of investigation.

The relations of the metal iron to carbonic oxide gas appear to be altogether peculiar. They cannot fail to have a bearing upon the important process of *acieration*. The intervention of carbonic oxide in the usual process of the cementation of iron with charcoal, long recognized by accurate observers, may be said now to be placed beyond all doubt by the recent beautiful research of M. Margueritte.* Hitherto the decomposing action of the iron upon carbonic oxide has been supposed to be exercised only at the external surface of the metal. A surface-particle of the iron has been supposed to assume one-half of the carbon belonging to an equivalent of carbonic oxide (C_2O_2), while the remaining elements diffused away into the air as carbonic acid (CO_2), to re-acquire carbon from the charcoal placed near, and to become capable of repeating the original action. It is now seen that such a process need not be confined to the

* Ann. Ch. Phys. [4], vi. (1865).

surface of the iron bar, but may occur throughout the substance of the metal, in consequence of the prior penetration of the metal by carbonic oxide. The direct contact and action of carbon (in the form either of diamond or charcoal) upon iron is allowed to produce cast iron and not steel. It appears that the diffused action of carbonic oxide is the proper means of distributing the carbon throughout the mass of iron. The blistering of the bar appears to testify to the necessary production and evolution of carbonic acid, owing to the decomposition of the carbonic oxide in the interior of the bar.

The inquiry suggests itself whether acieration would not be promoted by alternation of temperature frequently repeated. The lowest red heat, or a temperature even lower, appears to be most favourable to the absorption of carbonic oxide by iron, or for impregnating the metal with that gas; while a much higher temperature appears to be required to enable the metal to decompose carbonic oxide, to appropriate the carbon, and become steel. The action of a high temperature is made very clear by M. Margueritte. The process of acieration, it seems then, should be divided into two distinct stages, conducted at very different temperatures,—the first to introduce carbonic oxide into the iron, and the second to decompose the carbonic oxide so introduced. The carbonic oxide once safely occluded by the iron, the metal might even be cooled and preserved in the air, the second heating being postponed for any length of time. Such alternations of temperature are not unlikely to occur by accident during the usual long process of cementation; but they might be properly regulated with advantage, and the process may admit of being abridged in point of time.

Antimony, as a highly crystallisable metal, was exposed to hydrogen gas both above and below the point of fusion of the metal, and afterwards submitted to exhaustion in the usual manner. No hydrogen was extricated.

XXIII.—*Oxidation of Formic Acid.*

By Ernest Theophron Chapman.

Formic acid is so common a product of the oxidation of organic bodies, that its behaviour with oxidizing agents is of great interest. In the old processes for its preparation, viz., by oxidation of starch, sugar, &c., an exceedingly violent reaction always takes place and a very small quantity of formic acid is obtained. If we moderate the violence of the reaction, still less formic acid is produced; for instance, when glycerin is oxidized with bi-chromate of potash and sulphuric acid, the products are either formic acid, carbonic acid and water, or carbonic acid and water only, the absence or presence of formic acid depending entirely on the concentration of the solution employed. With a dilute solution, at a rather low temperature, no formic acid whatsoever is produced; with a concentrated solution, however, a moderately large quantity of the acid is obtained. This result is doubtless due to the fact that at the high temperature produced by the action of glycerin on concentrated chromic acid, the formic acid is at once volatilized, or carried away by the carbonic acid, which is always simultaneously formed. From these circumstances it appears that formic acid, at any rate when in the nascent state, is completely decomposed by chromic acid. It is also completely decomposed when in the free state. About a gramme of formic acid was oxidized in an open vessel with excess of dilute chromic solution, the temperature never being allowed to rise above 40°. After about half an hour the solution was boiled, and a small quantity distilled. This distillate was carefully tested for formic acid, with the silver test. Not a trace could be discovered. Still, to put the matter beyond all doubt, the quantity of oxygen requisite to oxidize formic acid was determined, and also the amount of carbonic acid produced by the oxidation. The formic acid employed in the following experiments was weighed as formate of barium.

Determination of oxygen consumed—

$CHBaO_2$ taken = 0·7436 grm.

Standard chromic solution employed = 21·425 grm.

The formate was sealed up with the chromic solution and digested for half an hour in the water-bath. The contents of the tube were transferred to the generating flask,* and there boiled to expel carbonic acid. The amount of carbonic acid which the solution liberated with oxalic acid was then determined. Amount of carbonic acid liberated, 1·046 grm. 100 grms. of chromic solution liberate 7·5182 grms. of carbonic acid. Therefore 21·425 grms. would liberate 1·6107 of carbonic acid. Subtracting from this the amount actually liberated, viz., 1·046, we obtain ·5647.

By the proportion 88 : 16 : : ·5647 : x, we learn the amount of oxygen consumed, viz., ·10267 grm. Dividing this by the amount of formate employed, we obtain 13·807 as the percentage of oxygen consumed. Supposing the whole of the formate to have been converted into carbonic acid and water, we should have required 14·097. We have therefore employed 97·95 of the theoretical quantity. This result, although not so sharp as some mentioned in a previous paper, is still sufficient to show that the formic acid is practically all converted into carbonic acid and water.*

Determination of the carbonic acid evolved during the oxidation of formic acid:—

$CHBaO_2$ taken.....	11·5342	grms.
CO_2 liberated	4·471	„

Percentage of carbonic acid, therefore, 38·762
Theory requires .... 38·767

or 99·987 per cent. of the theoretical quantity.

This determination was made by mixing the solution of the formate with cold dilute chromic solution. The mixture was very slowly warmed, and the carbonic acid liberated, absorbed, and weighed.

From the above I conclude that formic acid will not withstand the action of chromic acid. It therefore differs *in toto* from the acids of the acetic series.

Laboratory of the London Institution.

* See paper entitled "Limited Oxidation: amount of Oxygen consumed," p. 180 of this volume.

XXIV.—*Note on the Synthesis of Formic and Hyposulphurous Acid.*

By A. Dupré, Ph.D.

The paper, "On a new Synthesis of Formic Acid," by Mr. Chapman, published in the March number of the Journal of the Chemical Society, has recalled to my mind some experiments performed by myself several years ago which may perhaps furnish another possible explanation of Mr. Chapman's results.

At that time I endeavoured to prove that formic and hyposulphurous acid were similarly constituted, and failing to obtain any volatile compounds of hyposulphurous acid from which its atomic weight could be derived, I directed my attention to the synthesis of these two acids.

Kolbe's synthesis of formic acid, by the action of potassium or sodium on carbonic acid, had then been just published, and on trying the same experiments with sulphurous acid and sodium, hyposulphite of soda was readily obtained.

$$2CH_2O_3 + 2Na = CHNaO_2 + CHNaO_3 + H_2O.$$
$$2SH_2O_3 + 2Na = SHNaO_2 + SHNaO_3 + H_2O.$$

If instead of taking merely the moist gases, an aqueous solution of the gases is acted on by sodium-amalgam, the reaction takes place even more readily. This formation of hyposulphurous acid might indeed have been anticipated, from the known formation of hyposulphite by the action of zinc on a solution of sulphurous acid. I now tried this latter reaction for the production of formic acid; but without result. The experiment was, however, performed at ordinary temperature only; by enclosing the aqueous solution of carbonic acid and the zinc in strong sealed tubes, and exposing them to a somewhat higher temperature, better results may perhaps be obtained.

I next hoped to produce formic acid by acting with an aqueous solution of an alkaline carbonate on carbon, analogous to the production of a hyposulphite by the action of sulphur on a sulphite.

$$Na_2SO_3 + S + H_2O = 2NaSHO_2.$$
$$Na_2CO_3 + C + H_2O = 2NaCHO_2.$$

At first I used ordinary charcoal, or carbon obtained by the ignition of bitartrate of potassa, which had been purified by boiling with acid, and strong ignition in air. The carbon was introduced into glass tubes together with a solution of carbonate of potassa or soda. The tubes were then sealed and heated in a water-bath for from 12 to 60 hours. If at the end of this time the tubes were opened, the carbon having been allowed to settle, and the clear solution was distilled with sulphuric acid, distinct traces of formic acid were always obtained. To obviate any objection as to the purity of the carbon employed, gas carbon was taken and carefully purified by ignition in air and in a current of chlorine gas. This carbon was introduced into a Papin's digester, silvered inside (carefully avoiding all contact with organic substances), and heated with a solution of pure carbonate of soda (strength about 15%), to a temperature of from 100 to 150°, and for periods varying from 2 to 14 days. The clear alkaline solution, when treated as above, still yielded distinct traces of formic acid in the distillate, readily detected by the ordinary tests (reduction of silver and mercury salts), but even several repetitions of the process never yielded me enough acid for analysis. Comparative experiments in which either the carbon and water, or the aqueous solution of carbonate were heated separately in the digester, yielded no trace of formic acid. Owing to my inability thus to obtain any quantity, I abandoned the experiments, nor would I now venture to bring them before the Society were it not in the hope of their perhaps throwing some light on Mr. Chapman's observations.

Finally, the above experiments render it at least probable that the formic and hyposulphurous acids are analogous in constitution, hyposulphurous acid being, in fact, formic acid in which the carbon is replaced by sulphur, or *vice versâ*. This view is further supported by the observation of Rose, according to whom, no hyposulphite is capable of existing which does not contain at least one atom of hydrogen. The atomic weight of hyposulphurous acid as at present adopted would then require to be reduced to one-half.

XXV.—*Experiments on Oxidation by means of Charcoal.*

By F. Crace Calvert, Ph.D., F.R.S.

It has been known to Chemists ever since the memorable experiments of Theodore de Saussure, that charcoal possesses the property of condensing many times its own volume of various gases, and in some instances, as in that of ammonia, or hydrochloric acid, from 80 to 90 volumes; but this property of carbon was considered as a mere physical property, until Dr. John Stenhouse's papers appeared in the "Chemist," for 1855 and 1857, in which he clearly demonstrated that carbon was a conveyer of oxygen to the various gaseous products emanating from substances in a state of putrefaction, and that all the putrid gaseous matters and vapours evolved from an animal buried in charcoal were so completely oxidized, that no unpleasant odour was perceptible.

These interesting results induced me to make a series of experiments with the view of ascertaining if, under such circumstances, the oxidation was carried to its maximum or not, and to what extent this mode of oxidation was applicable to organic compounds.

To carry out these views, I prepared pieces of boxwood charcoal as near 1 cubic inch in size as possible. These were treated with slightly diluted hydrochloric acid, and afterwards washed with distilled water, so as to remove from them all mineral matters, especially alkaline carbonates, as these might have interfered with the results, since acids are generally produced when oxidation is carried to its maximum. To ascertain the oxidizing power of condensed oxygen, a cube was dried and heated to redness, and whilst still red-hot, was introduced into a cylinder standing over mercury, and containing a measured volume of pure oxygen. It generally required 24 hours before condensation of the oxygen ceased, and it was only then that the gas to be oxidized was added, and the whole left until no further absorption was apparent. The

charcoal was then removed, and carefully tested for the products of oxidation formed.

Before however examining the action of charcoal containing condensed oxygen upon gaseous compounds, and especially organic substances, I considered it advisable to ascertain that no carbonic acid was produced by the contact of purified charcoal with oxygen. I therefore examined both fresh charcoal and some which had been in contact with oxygen, and the result in both cases was perfectly satisfactory, for no carbonic acid had been formed or existed in the cube of charcoal.

1. I then brought moist sulphurous acid into contact with charcoal containing oxygen as described above, and found that it was very rapidly converted into sulphuric acid.

2. A cylinder graduated into 100 divisions, being filled with oxygen, and the hot charcoal introduced, it was observed that after 24 hours the absorption was equal to 44 divisions. Moist sulphuretted hydrogen was then introduced, so as to replace the volume absorbed, or up again to 100 divisions, and in 24 hours the absorption was 72 divisions; so that the charcoal had absorbed afresh, 28 volumes of oxygen under the influence of sulphuretted hydrogen. I further ascertained that considerable quantities of sulphuric acid had been produced through the oxidation of the sulphuretted hydrogen.

3. Several experiments were made with the view of oxidizing ammonia, but I regret to say without any definite result; but although no production of nitric acid could be observed, I would not affirm that ammonia was not partially oxidized, for in this case as in the former one, the total absorption of gas was greater after the addition of ammonia gas, than it was with oxygen alone.

These results and those cited in the case of the oxidation of sulphuretted hydrogen, prove that Saussure was incorrect in stating that a gas possessed the property of driving out of charcoal another gas which had previously been absorbed by that substance, and that this was especially the case when charcoal was placed in contact with a gas more soluble in water than the one previously condensed.

4. In the case of gaseous phosphoretted hydrogen, prepared by heating phosphorus with a strong alcoholic solution of potash, the absorption was rapid, and, as in the preceding cases, a greater volume of the mixture was condensed than when the

charcoal was in contact with oxygen alone. In this instance a considerable quantity of phosphoric acid was also formed.

5. A second series of experiments was made with the view of producing organic acids from their alcohols by means of oxygen condensed in charcoal. The cylinder was filled with oxygen and a cubic inch of purified charcoal, red-hot, was introduced. After 24 hours, a few drops of methylic alcohol were passed into the cylinder by means of a pipette, and after 72 hours, no further absorption being noticed, the charcoal was removed, and a liquid extracted from it, which was found to reduce rapidly silver solution, thus tending to prove that formic acid had been formed; but there is a doubt if this acid was the real product of oxidation, as we could not reduce the salts of mercury, nor detect the presence of an acid by means of litmus.

6. Positive results were, however, obtained with ethylic alcohol when I operated in exactly the same manner as with methylic alcohol; for in this instance considerable quantities of acetic acid were produced, which I proved by converting a part of it into cacodyle, and the rest into acetic ether.

7. I was also successful in obtaining valerianic acid from amylic alcohol.

8. Lastly, a series of experiments was undertaken with the view of ascertaining what was the action of condensed oxygen upon some of the hydrocarbons, when the following results were arrived at:—

Ethylene ($\mathrm{C_2H_4}$). Some of this gas was brought in contact with oxygen and charcoal, as other gases were in the preceding experiments, and when the absorption had ceased the products of oxidation were examined. Having failed to detect any solid or liquid products of oxidation (excepting water), such as oxalic acid, aldehyde, &c., the charcoal was placed into a small flask containing *boiled* water, and the gases evolved from it on boiling were passed through lime-water, when a copious precipitate of carbonate of lime was formed, showing that ethylene had been oxidized into carbonic acid and water.

9. I then tried propylene ($\mathrm{C_3H_6}$), prepared by heating iodide of allyl ($\mathrm{C_3H_5I}$) with mercury and hydrochloric acid, and here again carbonic acid was produced, but no acetic acid, although I fully expected that such a compound would have been formed.

10. Amylene ($\mathrm{C_5H_{10}}$) was treated in the same way, and also gave rise to carbonic acid; but I must add that, in this

case, some other product was generated, for although the smell of amylene was completely destroyed, still there was an odour of one of the amylic ethers; which of them, however, could not be ascertained, as the quantity produced was too small.

The difference of oxidizing power with which condensed oxygen acts on certain carburetted hydrogens, or on the hydrates of the same, their alcohols, is well worth the attention of chemists; for whilst in the latter case it acts by substitution, replacing the hydrogen of the organic substance, in the former it acts in its true character (viz., as the most powerful comburent agent known), oxidizing the carbon and hydrogen of the organic substance to its maximum, thus converting the carbon into carbonic acid, and the hydrogen into water.

These experiments show that oxygen condensed by charcoal, is a most powerful oxidizer; and the question arises, whether the oxygen, which we may assume is liquefied on the surface of the charcoal, acts as a mere solvent of the other gaseous or liquid products brought into contact with it, and thereby becomes susceptible of acting upon the elements composing such substances; or whether charcoal, which has condensed oxygen by mere molecular attraction, has still the additional power of condensing or liquefying a second gas if brought in contact with it, thereby bringing each substance or compound into such a condensed state, that chemical action can easily ensue, and give rise to the results mentioned in this paper. I must say that I am in favour of the latter view, and I hope, shortly, to be able to bring before the Society, a series of results which will substantiate my views upon this important chemical subject.

XXVI.—*Oxidation of the Acids of the Lactic Series.*

By Ernest Theophron Chapman and Miles H. Smith.

We have on a former occasion shown that one of the secondary acids of the lactic series yields a ketone on oxidation. As might

have been expected, this is a general reaction. It appears in fact that all the acids of the lactic series yield either aldehydes or ketones; the primary acids aldehydes, and the secondary ones ketones. With Frankland and Duppa, we divide the acids into primary and secondary, accordingly as they contain hydrogen and an alcohol-radicle, or two alcohol-radicles. In either case the acid appears to be capable of being acted on by 1 eq. of oxygen, according to the following general equation:—

$$\left\{ \begin{matrix} C \left\{ \begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \end{matrix} \right\} HO \\ COHO \end{matrix} \right\} + O = C \left\{ \begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \end{matrix} \right\} O + H_2O + CO_2.$$

In this formula m and n are positive integers, or one of them may be equal to nothing. In the former case a ketone is produced, in the latter an aldehyde. The examples on which we ground this general statement are—

1st. *Lactic Acid.*—The products of the oxidation of this acid have been known for many years, and have been confirmed by us in a recent paper. In this case $n = 1$ and $m = 0$.

2nd. *Dimethoxalic Acid.*—This compound yields, on oxidation, acetone and carbonic acid. In this case m and n both equal 1. The acetone was recognised by its boiling point, by its compound with bisulphite of soda, and by its yielding acetic and carbonic acids on oxidation.

3rd. *Ethomethoxalic Acid.*—This compound was obtained from the corresponding ether, which had been prepared in the manner described by Frankland and Duppa. We found it quite impossible to get the ether at a constant boiling point. It evidently contained diethoxalic ether, from which we failed in entirely separating it. 28 grammes of the impure ether were digested with slight excess of caustic potash, and the resulting alcohol was distilled off. The crude potash-salt so obtained was rendered acid with sulphuric acid, and then warmed with 200 cc. of the 10 per cent. chromic solution. As soon as the reaction had commenced, the source of heat was removed. Large quantities of carbonic acid were evolved, and a liquid having a fragrant smell, resembling that of propione, distilled over, accompanied by water. This liquid was separated by means of the separating funnel, and the aqueous portion saturated with

chloride of calcium and partially distilled, whereby more of the fragrant liquid was obtained. As we shall prove below, this liquid is a ketone, viz., methylated acetone. As originally obtained, it was contaminated with a small proportion of propione, derived doubtless from the diethoxalic acid which accompanied the ethomethoxalic acid. From this it was separated by fractional distillation. It is a colourless liquid, with a smell strongly resembling that of propione, though distinctly differing from it. It boils between 82—83° C. A combustion of it with oxide of copper furnished the following numbers :—

Substance employed.	CO_2 found.	H_2O found.
0·2475	0·6065	0·2545

From these data the following percentages are calculated :—

	Theory.		Found.
C_4	= 48	66·67	66·83
H_8	= 8	11·11	11·4
O	= 16	22·22	—
	72	100·00	

From these numbers it appears that the substance still retained a trace of propione.

This substance combines with bisulphites, and evolves considerable heat in doing so. The compound formed, however, is very soluble in water, and is decomposed at the temperature of the water-bath.

On oxidation this substance furnishes nothing but acetic acid; this was proved by digesting a small quantity of it with bichromate of potash and dilute sulphuric acid, distilling out the acid formed, converting it into a baryta-salt, and determining the percentage of barium.

From the above it appears that ethomethoxalic acid splits up under the action of oxidising agents in a manner exactly analogous to diethoxalic acid :

$$\left\{ \begin{matrix} C \left\{ \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} \right\} HO \\ COHO \end{matrix} \right\} + O = C \left\{ \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} \right\} O + H_2O + CO_2, \text{ and}$$

$$C \left\{ \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} \right\} O + O_3 = 2C_2H_4O_2.$$

Therefore this acid also conforms to the general formula. In its case, $n = 2$ and $m = 1$.

The last example we shall bring forward is diethoxalic acid, for which both n and $m = 2$. We showed on a former occasion that this acid also follows the general formula.

From this it would appear that in the oxidation of the secondary acids of the lactic series, we possess a new general method for the formation of the ketones, and as there is no difficulty in the preparation of these acids—a method which will in all probability be resorted to, should the ketones be required as the basis of an investigation.

The facts that the normal acids of the lactic series, when oxidized yield an aldehyde containing 1 eq. of carbon less than the acid from which it was obtained, and that this aldehyde, on further oxidation, will yield an acid of the same number of atoms of carbon as itself possesses, furnish, we think, a most important means of investigating the problems of isomerism amongst the fatty acids. The method we should propose would be, first to prepare a bromine substitution-compound of the acid. This, as is well known, can be easily transformed into the corresponding lactic acid. By oxidizing this lactic acid, we should obtain an aldehyde, and then an acid containing 1 eq. less of carbon than the acid with which we started, provided that there is no irregularity in the linking of the terminal atoms of carbon. In this case we should obtain a ketone instead of an aldehyde, and the ketone, of course, could not yield an acid containing the same number of atoms of carbon as itself. For instance, there are two isomeric butyric acids, the normal one which may be represented thus—

$$\left\{\begin{matrix}CH_2CH_2CH_3,\\COHO\end{matrix}\right.$$

and the abnormal one, which may be represented thus—

$$\left\{\begin{matrix}CH\left\{\begin{matrix}CH_3\\CH_3.\end{matrix}\right.\\COHO\end{matrix}\right.$$

If in these two acids we substitute hydroxyl for hydrogen in the terminal methyls, we shall obtain two isomeric lactic acids, viz., hydr-ethoxalic acid,

$$\left\{\begin{matrix}CH_2CH_2CH_2HO\\COHO\end{matrix}\right.,$$

and dimethoxalic acid—

$$\left\{\begin{matrix} CH\left\{\begin{matrix} CH_2HO \\ CH_3 \end{matrix}\right. \\ COHO \end{matrix}\right. .$$

These formulæ differ only in form from those ordinarily given for the two acids named, viz., hydr-ethoxalic acid,

$$\left\{\begin{matrix} C\left\{\begin{matrix} C_2H_3 \\ H \end{matrix}\right\}HO, \\ COHO \end{matrix}\right.$$

and dimethoxalic acid—

$$\left\{\begin{matrix} C\left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\}HO. \\ COHO. \end{matrix}\right.$$

On oxidation, these two acids would yield respectively propionic aldehyde and acetone, besides carbonic acid and water. The molecular difference in the two butyric acids would thus be brought out in the clearest possible light.

The value of this course of proceeding is perhaps hardly obvious in the case of the isomeric butyric acids. When, however, it is applied to valerianic acid, and to its isomer, isopropacetic acid, the use of the process will at once become obvious. In this case the first operation would yield us two lactic acids, propyl-lactic acid or hydro-propyloxalic acid,

$$\left\{\begin{matrix} C\left\{\begin{matrix} CH_2CH_2CH_3 \\ H \end{matrix}\right\}HO, \\ COHO. \end{matrix}\right.$$

and hydro-pseudopropyloxalic acid—

$$\left\{\begin{matrix} C\left\{\begin{matrix} CH\left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\} \\ H \end{matrix}\right\}HO. \\ COHO \end{matrix}\right.$$

These two acids would yield on oxidation, besides carbonic acid and water, the first, normal butyric acid, and the second, pseudo-butyric acid, two substances with well-defined differences, and which could, were it thought needful, be made to show their structural differences by a repetition of the process.

We may remark that in their paper describing isopropacetic acid, Frankland and Duppa state that the only differ-

ence, physical or chemical, that they have been able to detect between it and ordinary valerianic acid consists in its different action on polarized light. Had this acid been met with in any reaction which did not furnish a direct clue to its constitution, it would have been regarded simply as valerianic acid. This sufficiently shows the necessity of an analytical method of investigating these acids.

London Institution Laboratory, April 16th, 1867.

XXVII.—*On Limited Oxidation with Alkaline Permanganate.*

By Ernest Theophron Chapman and Miles H. Smith.

Preliminary Notice.

The action of permanganic acid on organic bodies differs altogether according as it takes place in acid or in alkaline solutions.

If alcohol be treated with permanganate of potash and sulphuric acid, we obtain aldehyde and acetic acid, exactly as in the case of chromic acid. If however, we employ solution of crystallized permanganate, we obtain small quantities of aldehyde and acetic acid, together with various other bodies, and oxalic acid. If the permanganate be rendered strongly alkaline with potash, no aldehyde and no acetic acid whatever are produced, though the permanganate is almost immediately discoloured and binoxide of manganese is precipitated. If the solutions have been used hot, oxalic acid is the principal product; if cold, various other acids, probably identical with those obtained by Debus in his oxidation of alcohol by nitric acid, are produced. To obtain the oxalic acid, the alkaline solution is filtered, the filtrate rendered acid with acetic acid, and chloride of calcium added. Oxalate of lime was precipitated, and from it, all the reactions of oxalic acid may be obtained. It was analysed and proved to be pure.

In the case of lactic acid, similar results are obtained. With permanganate of potash, aldehyde, acetic acid, carbonic acid, and oxalic acid are all produced. With permanganate of potash and sulphuric acid, we obtain aldehyde, acetic acid, and carbonic

acid, exactly as when chromic acid is employed, and if we take permanganate and caustic potash, oxalic acid is produced, but no aldehyde and no acetic acid.

Oxalic acid itself appears to be totally unaffected by boiling with permanganate of potash and potash. I think the above facts will go far to explain the anomalous results obtained by M. Truchot in his oxidation of amylene. M. Berthelot has since oxidized amylene in a similar manner. He appears to have obtained acids of the acetic series and also bibasic acids. Had he employed alkaline solution of permanganate, he would have obtained no acetic acid whatsoever. Manganate is incapable of producing acetic acids. Manganic acid, however, in the free state is quite capable of producing these acids, and in fact produces no others.

If we consider what must take place when permanganate is reduced, we arrive at an explanation of these anomalies. If two solutions of permanganate, to one of which excess of caustic potash has been added, be reduced by the gradual addition of alcohol, totally different effects are observed. The alkaline solution rapidly becomes green, and for a considerable time no binoxide of manganese is deposited. The neutral solution, on the contrary, does not suffer this change of colour at all, but begins to deposit the binoxide at once. The neutral permanganate becomes green towards the end of the process only, and not even then, unless the reduction has been very slowly effected in a cold solution. The fact is, the neutral permanganate is, by the abstraction of 1 eq. of oxygen, in the presence of water, converted into 1 eq. of manganate of potash and the elements of 1 eq. of hydrated manganic acid. We say the elements, because hydrated manganic acid at once splits up into binoxide of manganese and oxygen. From this it appears that two-thirds of the available oxygen of the permanganate may be removed without in any way affecting the neutrality of the solution. But, as in this reduction acids are formed, an even larger quantity of oxygen may be removed from the permanganate before the solution has become really alkaline, and therefore before the decomposition has become perfectly regular. We have in fact, in this case, a most complicated series of actions; first, action in a neutral solution; secondly, action in a solution which may possibly have become acid from the products formed; and thirdly, action in an alkaline solution. All

these actions differ, and the result is, a complicated series of products.

Even in the case of the alkaline solution, we are not operating under one set of conditions; for some substances, citric acid for instance, will reduce permanganate under these circumstances to manganate, but have no action on the manganate so produced. From this it would appear that the only way to obtain a regular action is to employ manganate, and not permanganate. We may then hope to obtain definite and simple products, and shall in all probability find that they bear a definite and simple relation to the compounds from which they were produced.

Laboratory of the London Institution.

XXVIII.—*On the Presence of Soluble Phosphates in Cotton Fibre, Seeds, &c.*

By F. Crace Calvert, F.R.S.

The presence of phosphates in seeds has been known to chemists for a long period, and their existence in larger quantities in the seed, as compared with the amount in the other parts of plants, is also a well ascertained fact; and it is generally admitted by chemists that the presence of such phosphates can only be detected, and their amount ascertained, by first destroying the organic matter, and liberating the phosphates together with other mineral compounds constituting the ashes of plants.

The results of the experiments which I am now going to describe, tend to prove that the greatest part, if not the whole of the phosphoric acid or phosphates which exist in seeds is in a free state, that is to say, that they are retained only mechanically by the organic substances of the seed and its outer envelope, in the same manner as a piece of linen dipped in a solution of chloride of sodium mechanically holds the salt when the solvent is evaporated.

The researches contained in this paper were undertaken in consequence of some cotton-yarn being sent to my laboratory, to ascertain if any impurity had been introduced with a view to weighting it.

To ascertain this, a portion of it was steeped for several hours in distilled water, and the solution thus obtained was

carefully analysed by my assistant, Mr. A. C. Bowdler, who discovered in it a large quantity of magnesia.

Our first impression was, that chloride of magnesium had been introduced with the view of imparting weight to the cotton yarn, owing to its hygroscopic properties; but failing to obtain a sufficient amount of chlorine, or even of sulphuric acid, (in case sulphate of magnesia had been employed,) to account for the quantity of magnesia existing in a solution obtained from a given weight of fibre, we were induced to pursue our researches, when we detected a large quantity of phosphoric acid, which led us to believe that the cotton-yarn had not been artificially weighted with the magnesium-salt, but that the magnesia and phosphoric acid extracted from the cotton yarn, must exist naturally in the fibre.

A few rough experiments made on that point confirmed this view, and I therefore determined to institute a series of experiments, the first part of which I have now the pleasure of laying before the Society.

Seven samples of cotton wool were obtained from one of the first brokers in Liverpool. They were carefully carded at one of our cotton mills in Manchester, to remove all seeds or impurities that they might contain. In order to obviate every chance of influence of the climate or soil upon the results obtained, I selected samples of cotton, which had been produced in various parts of the world; thus I operated upon cotton from Egypt, New Orleans, Bengal, Surat, Carthagena, Macao, and Cyprus.

100 grammes of each sample of cotton were washed with pure distilled water until all traces of mineral matter were removed. These solutions were then evaporated to dryness and the residue calcined with a little carbonate of soda and nitrate of potash, and in this calcined mass the amount of phosphoric acid was estimated as phosphate of uranium.

The following are the results obtained:—

100 grammes of	Egyptian	cotton	gave	·055	PO_5.
„	Orleans	„	„	·049	„
„	Bengal	„	„	·055	„
„	Surat	„	„	·027	„
„	Carthagena	„	„	·035	„
„	Maceio	„	„	·050	„
„	Cyprus	„	„	·050	„

These results show that phosphoric acid is a constant constituent of cotton fibre, from whatever part of the world it is obtained; and that out of seven samples that we examined, five contained the same quantity of PO_5, viz., ·05 per cent.

I then made the following experiments to ascertain if the phosphoric acid ever was really combined with magnesia. I washed a quantity of clean carded Cyprus cotton with water until all the salts were extracted. The solution was then evaporated, the residue dissolved in dilute nitric acid, and ammonia added; the precipitate formed was redissolved in acetic acid, and the lime precipitated by oxalate of ammonia. Afterwards, on adding ammonia in excess, a copious precipitate of phosphate of magnesia and ammonia was produced, and weighed as pyrophosphate. On the addition of phosphate of soda to the filtrate, a further precipitate was obtained, but too small to be estimated.

I may add that after all the soluble salts were extracted by water from the various samples of cotton, they were dried and burnt, and the ashes examined for phosphates, and that only a trace of phosphoric acid was found.

Although these results tend to prove that the phosphoric acid is really combined with magnesia, still I admit that they are not quite conclusive; but I intend, during the ensuing summer, to continue my researches and try to solve that problem.

I have also washed with hot distilled water, wheat which I had separated from the ear, and found in the concentrated aqueous solution, a large quantity of phosphoric acid and magnesia.

French beans in the pod yielded also to water, large quantities of phosphoric acid and magnesia.

Lastly the same compounds were detected in water in which the kernels of nuts and walnuts had been allowed to steep for 48 hours.

In conclusion, I beg to state that I hope to lay before the Society next winter a complete series of results, as I intend, during the ensuing summer, to estimate not only the amount of phosphoric acid and magnesia in various seeds, but also their relative proportions at different stages of their growth.

XXIX.—*Observations on the Weathering of Copper Ores.*

By John Spiller, F.C.S.

It is a well-ascertained fact, that the sulphur-ores of copper undergo a slow oxidation on exposure to air and moisture, becoming partially converted into sulphate of copper, the rapidity of this change being determined by the state of division of the ore, its degree of purity, and the heat of the weather during which the moist heap remains exposed.*

In conjunction with Professor A. H. Church, I have lately had an opportunity of investigating the changes naturally occurring in samples of Devonshire ore, which contained, besides copper and iron pyrites, variable quantities of spathic iron-ore and schistous minerals in admixture.

The ores in question are raised from neighbouring mines in the southern division of the county, and they contain respectively eight and nine per cent. of copper in the form of copper pyrites, with other ingredients in the following average proportions:—

Ores.

	I.	II.
Cupriferous pyrites	36	40
Spathic iron ore	10	14
Sand and schist, with a little mica and fluor-spar	54	46
	100	100
Metallic copper, per cent.	8	9

Tailings from the preceding Ores.

	A.	B.	C.
Cupriferous pyrites	12·1	4·1	3·7
Spathic iron ore	12·0	20·5	23·9
Sand, mica, schist, &c.	75·9	75·4	72·4
	100·0	100·0	100·0
Metallic copper, per cent.	2·9†	1·0	0·9

* Vide Gmelin (*Handbook*, vol. v, p. 427), Watts (*Dictionary*, vol. ii, p. 78), Bloxam (*Chemistry*, p. 347).

† In many localities a sample containing so high a proportion of copper would be considered an "ore." Tailings of this quality will, no doubt, be eventually reworked.

A sample of spathic iron from Exmoor, Devon, analysed by me in 1855,* was found to contain 12·5 per cent. of the carbonate of manganese, whilst the spathic iron existing in admixture with the above copper ores appears to contain from 9 to 9·6 per cent., since 100 parts of the sampled ore marked II. when treated with hydrochloric acid, furnished Mn_3O_4 from the solution, corresponding to 1·25 parts of carbonate of manganese; and the refuse or tailings, C, gave an amount indicating 2·3 parts of the same constituent. The carbonates of iron, lime, and a trace of magnesia, were as usual the remaining components of the spathic ore; their relative amounts were not, however, accurately determined.

The pure stream of water used for the washing and commercial preparation of these copper ores, when collected above the mines, was found to be perfectly free from sulphates, and to contain only 4·5 grains per gallon of total dissolved constituents, the greatest part of which was carbonate of lime. No metallic impurities could be detected in it. Immediately below the workings, the same stream of water gave an abundant precipitate with chloride of barium, and the carbonate of lime was found to have been entirely replaced by the sulphate, and there was, besides, a considerable accession of sulphate of lime. This, again, was augmented by the presence of sulphate of manganese, and of other metallic salts, so much, indeed, that the residue left upon evaporation of the water showed a great increase, and, when ignited, became perfectly black. The water now contained 15·3 grains of total dissolved constituents, according to Mr. Church's analysis, and 1·38 grains of this was sulphate of manganese.

In samples of water collected at various times below the mines, I invariably found much sulphate of lime, together with other sulphates, particularly those of copper, iron, manganese, and alumina. Their relative amounts varied very considerably; thus, at different periods, sulphate of copper occurred to the extent of 0·38, 0·43, and 1·25 grains per gallon, and the protosulphate of iron oscillated between the limits of 0·57 and 4·13 grains; and, in one instance, in water taken from a depositing pit close to the mine, I found as much as 55·6 grains of green vitriol per gallon, together with considerable quantities of the sulphates of alumina and manganese. Besides these dissolved

* Percy's Metallurgy, vol. ii, pp. 210 and 227.

impurities, variable quantities of copper pyrites ore, in a state of minute division, were held suspended in the water.

These results led me to examine more closely into the nature and extent of the changes which the ore itself undergoes on exposure to the air. One pound of the moist copper ore, which at the time of taking the sample (March, 1866) gave up to water no appreciable amount of soluble sulphates, and certainly *no trace of copper*, furnished, a year later, no less than forty grains of a mixture of metallic sulphates, the aqueous solution of which was blue from the presence of copper, and contained besides much manganese and a little iron. A sample of the miner's refuse mud (tailings A), collected in January, 1866, and then containing a mere trace only of sulphate of iron, was preserved for fourteen months in a wide-mouthed bottle tied over with a double fold of paper. Most of the water evaporated in the interim and the air had consequently access to the contents of the bottle. Tested again in March, 1867, there was much sulphate of copper formed, and, upon washing with water, sixty-four grains of a mixture of metallic salts was obtained from a pound of the ore. This mixture consisted of the sulphate of manganese (chiefly), with sulphate of copper, and smaller proportions of the sulphates of iron, alumina, and lime, ingredients identical with those detected by Mr. Church and myself on different occasions in the mine waters.

The conclusions established by these experimental observations have, in the first place, verified the oft-repeated assertion as to the change of the sulphide ores of copper into sulphate under the conjoint influences of air and moisture; and have besides indicated secondary reactions, in the course of which the metallic bases of associated minerals, particularly in the instances of spathic iron and aluminous schist, become converted into soluble sulphates at the expense of an oxidized portion of the sulphur contained in the ore. They point to the necessity of adopting some precautions (the use of chalk or lime, for instance) to avert the baneful influence of such metallic salts upon land irrigated by, or naturally subject to the overflow from, streams thus impregnated with mineral poisons. And, finally, they disclose the existence of vast quantities of waste cupriferous material, which it would be very desirable to attempt to utilize.

XXX.—*On Phosphide of Magnesium.*

By JAMES PARKINSON.

(Abstract.)

THE author has confirmed his former observations upon the properties of phosphide of magnesium.* Phosphorus vapour does not attack magnesium at a dull red heat, unless the metal is in a finely divided state, and then only with difficulty. In a current of carbonic acid and phosphorus vapour, the carbonic acid acts upon the magnesium at a lower temperature than the phosphorus vapour, and the whole of the magnesium filings may be easily oxidized, with simultaneous deposition of carbon, by simply keeping the heat below that required for the phosphorus vapour to attack it.

Magnesium filings mixed with an equal weight of amorphous phosphorus in coarse fragments, and quickly heated to redness in a long narrow-necked bulb-tube, burn vividly, and yield a uniform well fused phosphide resembling a clinker, very difficultly fusible, very hard and brittle. When freshly fractured, it is of a bright steel-grey colour and lustre, but tarnishes rapidly in the air, and falls first to a brown powder, afterwards to a permanent greyish-white bulky powder, consisting only of magnesia, with a trace of hypophosphite or phosphite, and products of corrosion of the glass tube. In a closed tube it is infusible, and sustains a red heat without alteration; and in an open tube, it is but slowly oxidized, and only on the surface. It decomposes water, with brisk evolution of phosphoretted hydrogen and separation of magnesia. The same decomposition takes place slowly on exposing the phosphide to moist air—dry air has very little action upon it. Hydrochloric acid dissolves it with brisk effervescence, and evolution of phosphoretted hydrogen. Dilute nitric acid decomposes it with violence. Dry hydrogen has no action upon it.

The phosphide was analysed by passing a slow current of moist air over it, and collecting the evolved phosphoretted hydrogen in a solution of nitrate of silver. The oxidized product was first heated with water, then with dilute hydrochloric acid, and filtered from a little silicious residue (resulting from the action of the ignited magnesium on the glass tube). The

* See page 126 of this volume.

acid solution acidified with nitric acid, was heated for some time; then diluted with water, mixed with chloride of ammonium and excess of ammonia, stirred, and set aside in order to determine whether any precipitate was formed; only a trace was however obtained, proving that no phosphate of magnesia had been formed in the combustion, or in the oxidation of the phosphide. Finally the magnesium was precipitated by phosphate of soda, collected, washed, dried, ignited, and weighed.

The precipitate formed in the nitrate of silver solution, was acidified with nitric acid, and heated gently below 180° Fahr., until entirely dissolved, and the silver was precipitated as chloride by hydrochloric acid. The filtrate mixed with more nitric acid was heated for some time; and the phosphorus was determined in the usual way, by precipitation with ammonia and sulphate of magnesia.

The percentage results show an excess of magnesium due to some magnesium being dissolved out of the silicide of magnesium formed in the combustion.

The following results, however, give the formula for this very unstable phosphide as PMg_3, the same as the so-called black stable phosphide, described by Mr. Blunt,* was said to contain:—

	Experiment.			
	I.	II.	III.	Theory.
Magnesium	54·38	54·61	53·46	52·94
Phosphorus	45·62	45·39	46·54	47·06
	100·00	100·00	100·00	100·00

XXXI.—*Researches on Gun-cotton. On the Manufacture and Composition of Gun-cotton.*

By F. A. Abel, F.R.S., V.P.C.S.

[From the Philosophical Transactions for 1866.]

The general designations of pyroxylin and gun-cotton have been applied, up to the present time, to the several products obtained by the action of nitric acid, either alone, or in admixture with sulphuric acid, upon cotton-wool. In the earlier papers on gun-

* Chem. Soc. J. [2], iii, 106.

cotton, published within a short period of the announcement (in 1846) of Schönbein's discovery of a substitute for gunpowder, the action of nitric acid upon cellulose was assumed by the several investigators to furnish one single definite product, to which different formulæ were assigned, based in some instances upon analytical results, in others upon the increase in weight sustained by the cotton on its treatment with nitric acid, or a mixture of nitric and sulphuric acids. Pélouze, who was the first to produce (in 1838) an explosive substance by the action of nitric acid on cellulose, originally believed this product to be identical with that which Braconnot obtained from starch by its solution in cold nitric acid and precipitation by water. But in November, 1846, that chemist published the results of experiments establishing decided differences between the two bodies. The conclusion which Pélouze then arrived at regarding the composition of pyroxylin, was founded upon the tolerably constant increase in weight (between 68 and 70 per cent.) of dry cotton-wool and paper, when submitted to the action of monohydrated nitric acid, either employed alone or mixed with an equal volume of concentrated sulphuric acid. He considered that nitric cellulose was the sole product of the reaction, and that it consisted of one equivalent of cellulose *minus* one equivalent of water, combined with two equivalents of monohydrated nitric acid, its formula being

$$C_{12}H_{11}O_{21}N_2\ (\ddot{C}_{12}H_{22}\ddot{O}_{21}N_4).$$

Not long afterwards, Pélouze published conclusions varying somewhat from the preceding. He fixed the increase sustained by cellulose, upon its conversion into pyroxylin, at between 74 and 76 per cent., and was led by these numbers and by direct analytical data obtained with pyroxylin, to regard the formula

$$C_{24}H_{17}O_{17},5NO_5\ (\ddot{C}_{12}H_{17}\ddot{O}_{21}N_5)$$

as correctly representing the composition of that substance. The increase in weight which cellulose should sustain, by conversion into a substance of that composition, would be 74·9 per cent., a number which corresponds closely with the results obtained in these later experiments of Pélouze.

Numerous researches on the composition of pyroxylin were instituted by continental and English chemists at about the period of Pélouze's experiments, and the following are some of the

formulæ assigned by different experimenters to gun-cotton, in 1846 and 1847*:—

Pélouze (1846)	$C_{12}H_{11}N_2O_{21} = C_{12}H_9O_9, 2(HO.NO_5)$.
Péligot.....	$C_{12}H_9N_3O_{24} = C_{12}H_9O_9, 3NO_5$.
Von Kirchhoff and Reuter.....	$C_{12}H_9NO_{14} = C_{12}H_9O_9, NO_5$.
Fehling	$C_{12}H_{10}N_2O_{20} = C_{12}H_{10}O_{10}, 2NO_5$.
Porret and Teschemacher.....	$C_{24}H_{16}N_8O_{56} = 2(C_{12}H_8O_8, 4NO_5)$.
Pélouze (1847)	$C_{24}H_{17}N_5O_{42} = C_{24}H_{17}O_{17}, 5NO_5$.
Schmidt and Hecker	$C_{12}H_5N_5O_{30} = C_{12}H_5O_5, 5NO_5$.
Gladstone	$C_{24}H_{15}N_5O_{40} = C_{24}H_{15}O_{20}, 5NO_4$.
W. Crum	$C_{12}H_7N_3O_{22} = \begin{cases} C_{12}H_7O_7, 3NO_5. \\ C_{12}H_7O_{10}, 3NO_4. \end{cases}$

Most of the published results of individual experimenters exhibit considerable variation among themselves, and in several instances the mean results are only approximately represented by the formula adopted.

The very considerable discrepancies presented by the results of independent investigations are unquestionably due, in part, to the difficulties which have to be encountered in attempts to obtain trustworthy analytical results from so highly explosive a material as gun-cotton. The methods of analysis which have been adopted have been almost as numerous as the formulæ deduced from their results; and in several instances the quantity of material operated upon has been too small to permit of the attainment of satisfactory results by methods in which the sources of error were not inconsiderable.

There is no doubt, however, that the different conclusions arrived at by many talented chemists with regard to the composition of gun-cotton, are to be mainly ascribed to the fact that the treatment of cotton-wool with nitric acid, or a mixture of nitric and sulphuric acids, has furnished, in the hands of different operators, products differing considerably in composition. That such is the case is clearly indicated by the statements made in several of the published researches with regard to the increase of weight sustained by the cotton upon treatment with acid. Thus Pélouze, in his first paper on the composition of

* The notation employed by the several experimenters is retained in this statement.

pyroxylin, states that he found the increase of weight constantly comprised between 68 and 70 per cent. In his next publication he fixes the increase of weight at between 74 and 76 per cent., the theoretical increase, according to the formula which he fixed upon, being 74·9 per cent.; and Von Kirchhoff and Reuter obtained an increase of 76 per cent. Gladstone also found the increase of weight to be between 73 and 76 per cent. Porret and Teschemacher obtained an increase of only 54 per cent.; Teschemacher afterwards found the increase to be 69 per cent. Gregory and Schmidt and Hecker arrived at a similar result; while W. Crum, whose experiments were made with very carefully purified cotton, obtained an increase of 78 per cent. The increase of weight which, in other instances, the cotton must have sustained, for the attainment of the analytical results quoted, must have been even more various: thus Ransome's results would indicate an increase of weight of only 65·4 per cent., while those of Péligot correspond to a gain of 94·4 per cent.

Other indications of differences in the characters of the products operated upon by different chemists are furnished by statements made with regard to the action of solvents upon them. Their solubility in mixtures of alcohol and ether evidently varied considerably; and in one instance of these earlier experiments (namely, those of MM. Ménarde and Domonte in 1846), a description of gun-cotton soluble in ether and alcohol was described as obtained, together with a proportion of an insoluble product. The analysis of the latter furnished results which correspond very closely to those demanded by the formula

$$C_{12}\left\{\begin{matrix}H_8\\2NO_4\end{matrix}\right\}O_{10}.$$

Béchamp instituted some researches upon gun-cotton in 1852, in which he obtained, by the action of ammonia upon a soluble form of gun-cotton, a substance to which he assigned the formula

$$C_{24}H_{17}O_{17},4NO_5\ (C_{24}H_{34}O_{17},4N_2O_5),$$

viewing it as pyroxylin from which one equivalent of nitric anhydride had been abstracted; he therefore considered that the formation of this substance confirmed Pélouze's view of the composition of gun-cotton.

It was believed by some chemists at about this period that pyroxylin was itself only slightly soluble in mixtures of alcohol and ether, but that these mixed solvents either modified its character or separated it into two distinct explosive bodies, the one being soluble and the other insoluble in the ether and alcohol. Others regarded the difference in solubility exhibited by gun-cotton, according to the manner in which it had been prepared, as ascribable to differences of molecular condition, and not of composition.

But all the early investigators of this subject appear to have agreed in the opinion that the action of nitric acid, or of the mixed acids, was completed in a few minutes, and that, however much the treatment with acids was protracted, no further change was effected.

Gerhardt, in his "Traité de Chimie Organique" (1854), states that, as no gas is disengaged in the production of pyroxylin (a point upon which Pélouze lays stress in his earlier papers), this substance may be affirmed to contain the elements of cellulose *plus* two or three proportions of the elements of nitric anhydryde, and that it may be represented as cellulose in which two or three atoms of hydrogen are replaced by their equivalent of peroxide of nitrogen. This view of the composition of gun-cotton, which was first enunciated by Crum, received very strong support from the interesting researches of Hadow, published in 1854. The experiments of this chemist furnished conclusive evidence of the possibility of producing four distinct varieties of pyroxylin, by submitting cotton-wool to the action of different mixtures of nitric and sulphuric acids. Moreover, by carefully determining the increase of weight sustained by the cotton upon immersion in acid mixtures of different composition, and also by applying a new process to the examination of the products, Hadow succeeded in establishing the composition of three of these substances.

By repeated immersion of pure cotton in a mixture of the strongest sulphuric and nitric acids, Hadow obtained an increase of 81·34 per cent., a number considerably higher than that obtained by previous experimenters, and nearly corresponding to the theoretical gain (83·3 per cent.) which cotton would sustain by its conversion into a product of the formula

$$C_{18}H_{21}O_{15}, 9NO_2, \text{ or } C_6\left\{\begin{matrix}H_7\\3NO_2\end{matrix}\right\}O_5, \text{ or } C_{12}H_{14}O_7, 3N_2O_5 (C_{36}H_{21}O_{30}, 9NO_4, \text{ Hadow}).$$

By determining, in the form of nitric acid, the oxide of nitrogen contained in the product, and reproducing the cotton from the latter by the action of potassic sulphhydrate, Hadow, moreover, obtained numerical results closely agreeing with those which should be furnished by trinitro-cellulose or trinitric cellulose, and therefore confirmatory of the conclusion which was based upon the weight of the product furnished by as complete a treatment as possible of the cellulose with the strongest nitric and sulphuric acids. Similarly, Hadow established the composition of two lower nitric products, having respectively the formulæ

$$C_{18}H_{22}O_{15}, 8NO_2 \; (C_{36}H_{22}O_{30}, 8NO_4),$$

and

$$C_{18}H_{23}O_{15}, 7NO_2 \; (C_{36}H_{23}O_{30}, 7NO_4),$$

and differing from the highest compound in being soluble in mixtures of ether and alcohol.

Not long after Hadow's researches were made known, Béchamp published a continuation of his experiments with soluble gun-cotton. In this paper he adheres to the conclusion that Pélouze's formula for pyroxylin ($C_{24}H_{17}O_{17},5NO_5$) is correct, because he obtains, by the action of ammonia and potassa upon that substance, products the composition of which he represents by the formulæ

$$C_{24}H_{17}O_{17}, 4NO_5 \text{ and } C_{24}H_{17}O_{17}, 3NO_5.$$

Redtenbacher, Schrötter, and Schneider, in a joint report prepared by them in 1863 on gun-cotton manufactured by Baron von Lenk, adopted the view that the most explosive variety of gun-cotton was trinitro-cellulose, and quoted several satisfactory analytical results in proof of their assertion that gun-cotton, prepared according to Lenk's directions, was that substance in a nearly pure state.

The composition of the most explosive gun-cotton was indeed very generally regarded as definitely established to be trinitro-cellulose, or trinitric cellulose, until the publication (in 1864) of the memoir of Pélouze and Maury, in which that view is combated, and a new formula,

$$C_{24}H_{18}O_{18}, 5NO_5 (C_{24}H_{36}O_{18}, 5N_2O_5),$$

is assigned to that substance, which differs, by the elements of one equivalent of water, from Pélouze's second formula, adopted in 1847.

Some analytical results are referred to by Pélouze and Maury in support of their view of the composition of gun-cotton; but they base their new formula principally upon the increase of weight which they have found cotton to sustain by treatment with the mixed acids, and which they now fix at 78 per cent. (the numbers formerly arrived at by Pélouze being from 68 to 70 and from 74 to 76 per cent.). The theoretical increase of weight which *pure cellulose* should sustain upon complete conversion into a substance of the composition assigned to it by Pélouze and Maury is 77·78 per cent.; while, if gun-cotton were completely converted into trinitro-cellulose, it should gain in weight 83·3 per cent.

It would appear that these numbers are sufficiently far apart to preclude any uncertainty with regard to the correctness of a conclusion in favour of either formula, if based upon careful and sufficient experiments. Nevertheless, Pélouze and Maury state, on the one hand, that they base their somewhat complex formula upon the results of many experiments, variously instituted; while, on the other hand, the results arrived at by Hadow, which are not in any way referred to by Pélouze and Maury, and have never yet been called into question, appear to furnish very strong evidence in favour of the more simple formula.

Early in 1863, by desire of the Secretary of State for War, I entered upon a detailed investigation of the manufacture of gun-cotton, the composition of the material when produced upon an extensive scale, its behaviour under circumstances favourable to its change, and other subjects relating to the chemical history of this remarkable body.

The continuation of these investigations was afterwards entrusted to me by my colleagues, upon the appointment of a Government Committee on Gun-cotton.

The circumstance that the manufacture of the supplies required for the artillery and other experiments has been carried on under my direction, has enabled me to institute numerous experiments upon a considerable scale, in some of which the conditions of manufacture have been varied, while in others the quantity of product furnished has been carefully determined.

By combining such experiments with a very extensive series of analytical and synthetical laboratory investigations, I have endeavoured to render both rigorous and exhaustive the examination into the uniformity of the process of manufacture of gun-cotton as perfected by Von Lenk, and into the composition of the product.

I.—Manufacture of Gun-Cotton.

The present system of manufacture of gun-cotton does not, at first sight, present any important features of novelty, when compared with the methods of operation prescribed by Schönbein, Böttger, Otto and others, and pursued upon an extensive scale, for a short time, at Messrs. Hall's gunpowder works, and at Bouchet. Acids of the specific gravity prescribed by Von Lenk and mixed in very similar proportions to those which he indicates, were employed;—in some instances the cotton was submitted to a preliminary purification, as directed by him, and the product, after being washed in water, was also submitted to treatment with an alkaline bath, the mode only of carrying out this process of purification differing somewhat from that which Von Lenk adopts. But the application, upon a manufacturing scale, of the system which has been pursued under Lenk's direction at the manufactory at Hirtenberg, brings to light several details of considerable value, the adoption of which unquestionably ensures the attainment of greater uniformity and purity of the product of manufacture than could be secured by the earlier modes of operation.

The important steps in Von Lenk's system of manufacture are briefly as follows:—

1. The carded cotton is spun into a loose yarn, varying in size and strength according to the applications it is to receive; and the yarn is made up into hanks of convenient size (weighing about three ounces).

2. The cotton is submitted to preliminary purification by boiling it for a few minutes in a solution of potassic carbonate, of specific gravity 1·02, separating the alkaline liquid by means of a centrifugal extractor, and washing the cotton thoroughly in water.

3. The cotton is perfectly dried by artificial heat, immediately before its treatment with acid.

4. The acid used for the production of the gun-cotton is prepared by mixing one part by weight of nitric acid, of specific gravity 1·52, with three parts of sulphuric acid of specific gravity 1·84. This mixture is allowed to become perfectly cold before use.

5. The dry cotton is immersed by small quantities (about six ounces, or two hanks, at one time) in a bath of the mixed acids, which is kept as cool as possible. When the cotton has become thoroughly saturated and has been moved about in the acids for a few minutes, it is removed from the bath to a ledge placed over it, where a portion of the acid absorbed is separated by gentle pressure; the hanks are then transferred to small covered stoneware vessels, in which they are preserved for forty-eight hours, the proportion of acid with which they are allowed to remain saturated for that period being 10·5 parts by weight to 1 of the original cotton. The vessels containing the gun-cotton and acid are kept as cool as possible by being surrounded with water.

6. The acid removed from the bath by each successive quantity of cotton immersed, is replaced by the addition of a corresponding quantity of the fresh mixture, before another quantity of cotton is treated.

7. After the lapse of forty-eight hours, the acid is separated from the gun-cotton as completely as possible by mechanical means (*i. e.* by means of the centrifugal extractors). The expressed acids are not employed again.

8. The hanks are then drenched with water, singly, as rapidly as possible; they are afterwards washed by hand until no longer acid to the taste, and are afterwards placed in crates or perforated boxes and kept immersed in flowing water for about three weeks.

9. At the expiration of that time the water is separated mechanically from the gun-cotton, and the moist skeins are boiled for fifteen minutes in a solution of potassic carbonate of specific gravity 1·02. When the alkaline liquor has been expressed, the skeins are once more immersed in flowing water for a few days; the finished gun-cotton is then dried by exposure to air.

10. It is afterwards allowed to soak for about one hour in a cold solution of sodic silicate of specific gravity 1·072. The liquid is then expressed from the hanks in the usual manner; after

which they are allowed to dry thoroughly, again washed for five or six hours in running water, and finally by hand. The thorough desiccation of the gun-cotton then completes its manufacture.

The employment of the cotton in the form of hanks of loosely spun yarn, instead of simply in the loose carded condition, considerably facilitates its conversion and purification. The proper impregnation of the cotton by the acids is more rapidly accomplished with the hanks; such manipulations as attend the separation of the main quantity of acid from the converted material, and its first rapid and complete immersion (while still saturated with the concentrated acids) into water, are much more readily carried out with the cotton in the spun form; and, again, the exposure of the latter to the full purifying effects of a current of water is much more simply and perfectly effected than if carded cotton be used, while the mechanical loss of wool and of gun-cotton, in the several operations of washing and expressing, is much reduced.

The preparation of the mixture of nitric and sulphuric acids, as directed by Von Lenk, involves no important point of novelty; the necessity of employing the mixture cold, and therefore of either submitting it to refrigeration before use, or preparing a stock of the mixture some time before it was required, was well known to the earlier operators.*

In the treatment of the cotton with the mixed acids, the following precautions, viz., the immersion of uniform quantities of the perfectly dry cotton in the bath of acid, the adherence to

* An observation made by Béchamp, in his papers on Pyroxylin, that the production of a soluble or an insoluble product was determined simply by conditions of temperature, when the conversion was effected by means of sulphuric acid and saltpetre, induced me to ascertain by experiment whether the solubility, in alcohol and ether, of the product obtained with the employment of the prescribed mixture of nitric and sulphuric acids, increased, if the temperature of the latter was raised to about 70° C. That temperature was fixed upon for the experiment, as being the average of the freshly prepared mixture of nitric and sulphuric acids, usually employed for producing gun-cotton for photographic purposes, and which, in experiments instituted, furnished soluble gun-cotton yielding transparent collodion. The products obtained by the action of the warm mixture upon the cotton-wool exhibited no difference as regards its insolubility, from the ordinary products furnished by the cold mixture. Neither was insoluble gun-cotton rendered at all soluble by being submitted to treatment with the warm mixture. Hadow has shown that a more dilute mixture of acids which, when cold, furnishes an almost insoluble product, will, if employed at a temperature of 55° C., yield perfectly soluble gun-cotton, giving a fluid transparent collodion.

a fixed proportion in weight between the cotton and the acid with which it is left in contact, and the regular replacement of the acids removed from the bath at each successive immersion of cotton, by a corresponding quantity of fresh mixture, combine to exert no unimportant influence upon the uniformity of the product. That such is the case has been established by manufacturing experiments. For example, on one occasion some hanks of cotton were immersed in the bath of acids without addition to the latter of the quantity of fresh acid proportionate to the amount removed in the previous operation of immersion. The resulting product, which was in all other respects treated as usual, exhibited a decided difference, both in its composition and its explosive powers, when compared with gun-cotton previously produced, strictly according to rule, in the same bath of acids.

As regards the period during which the cotton is allowed to remain immersed in the acids, the precise time fixed upon by Lenk (48 hours) appears to be arbitrary, but there is good reason for prolonging for several hours the contact between the acids and the product. That a few minutes' immersion of a small quantity of cotton may be sufficient to convert it into a highly explosive and even to a great extent into the most explosive product, is indisputable; but a considerable period elapses before the cotton, especially when it is spun and when at least 6 ozs. are operated upon at one time, is converted, as *completely as possible* by one single treatment, into the most explosive product.

In operating upon small quantities of cotton, when the proportion of acids employed is always considerably in excess of that prescribed by Von Lenk, an immersion of the cotton for two hours has been found to furnish results quite as perfect as those obtained by protracting the immersion for 48 hours. Even when the proportion of acid to cotton was reduced, in small experiments, as nearly as possible to that employed in a manufacturing operation, the results of 12 and 24 hours' immersion were quite equal to those produced by treatment for the full period; indeed, decided evidence was obtained that the very long-continued contact of gun-cotton with the acids gave rise to a slight loss, a small proportion of the product being eventually dissolved by the acids. But when the duration of the treatment of even small quantities of cotton (between

three and four grammes) with a large excess of acid was limited to ten minutes, the conversion was comparatively very imperfect, and the products contained considerable proportions of soluble gun-cotton.

A careful examination of products of manufacture, prepared by continuing the contact of the acids with the gun-cotton for only one-half of the usual period (twenty-four hours), failed to indicate any difference between them and products obtained by the full period of immersion; on the other hand, a prolongation of the immersion to seventy-two hours did not furnish results more closely in accordance with theoretical demands than the ordinary treatment.

It was found, by experiments with several hundred pounds of spun cotton, that a considerable increase beyond the prescribed proportion of acid left in contact with the gun-cotton (eighteen or twenty parts instead of ten parts to one of cotton) furnished products which differed from those obtained by a strict adherence to Lenk's directions, only in containing somewhat smaller proportions of foreign matters than products in the manufacture of which ten parts of acid had been used.

The heat resulting from the chemical action of the nitric acid upon the cotton, and from the union of the acids with the liberated water, is considerable; it is therefore quite as important that the bath of acid in which repeated immersions are effected should be kept cool by being surrounded with cold water, as that the acid mixture should, in the first instance, be perfectly cold. Moreover, the precaution which Von Lenk adopts (excepting in cold weather) of keeping the closed vessels, in which the gun-cotton remains for forty-eight hours in contact with the acids, surrounded by cold water, is also very essential; for otherwise the accumulation of heat by the contents of the vessel, in consequence of the gradual conversion of some portions of the cotton, after its removal from the bath, may occasionally become sufficiently considerable to establish a destructive action of the acids upon the gun-cotton.

There can be no question as regards the necessity of employing some method, such as that adopted by Von Lenk, for rendering as sudden and complete as possible the first immersion into water of the gun-cotton which is still saturated with acids (though these have been separated from it as far as possible by means of a centrifugal extractor); for if the hanks

are simply thrown or dipped into water, the heat generated by the gradual penetration of the latter into the compact mass of gun-cotton, saturated with concentrated acids, suffices to establish in some parts a destructive action of the latter upon the gun-cotton, which is rendered evident by the disengagement of nitrous vapours, and which, though it is very speedily checked, as the acid becomes largely diluted by water, may give rise to the production of small quantities of substances of comparatively unstable character, not removed from the gun-cotton by the subsequent purification. The most effectual plan of rapidly diluting the acid in the gun-cotton is to throw the skeins just removed from the extractor singly *into* a cascade of water, whereby the instantaneous penetration of the mass of cotton by a large body of water is accomplished with ease and certainty.

The subsequent continuous immersion of the gun-cotton for at least three weeks in a stream of water, as directed by Von Lenk, is unnecessarily long, as the gun-cotton is afterwards still subjected to treatment with an alkaline water, and to a final washing. In the manufacturing operations carried on at Waltham Abbey, where only a very slow stream of water was available for the purposes of purification, the period for which the gun-cotton was allowed to remain in the water, after the preliminary washing in the cascade, was, in some instances, forty-eight hours, in others from ten to fourteen days. There is no question that the latter period was excessive, especially with the improved methods there adopted of exposing the gun-cotton to the purifying action of the water. Indeed there can be no doubt that this first washing is of minor importance, as affecting the ultimate purity of the product, compared to the treatment with alkaline liquid which it receives, and which, according to Von Lenk's directions, consists in boiling the gun-cotton for about fifteen minutes in a solution of potassic carbonate of specific gravity 1·02. The gun-cotton, manufactured nearly three years ago at Waltham Abbey, which was submitted to a first washing of only forty-eight hours, but was washed for a fortnight after treatment with alkali, has proved in every respect equal in permanence to products of more recent manufacture which have been submitted to the long-continued first washing. The curtailment of this washing operation, if compatible with perfect security, would be im-

portant, not only on account of the time saved in the manufacture, but also because, if the gun-cotton remains immersed in spring- or river-water in localities where light cannot be perfectly excluded, vegetable growth is speedily established upon it, and the perfect separation from it of extraneous organic matter becomes afterwards a very difficult and time-consuming operation. But, although the perfect permanence, for a period of nearly three years, coupled with very great power of resisting the destructive effects of heat and light, possessed by products in the manufacture of which the long-continued washing was postponed until after the alkaline treatment, warrant the belief that this method of operating secures the proper purification of the product, I have obtained indications, in other manufacturing operations, that a very considerable curtailment of the *total* purification, by washing, which the gun-cotton receives, in addition to the treatment with alkali, somewhat diminishes its power of resisting destructive influences. The omission of the treatment with an alkaline bath affects to a much more decided extent the permanence of the gun-cotton; indeed it is doubtful whether, even if the washing were protracted considerably beyond the full time prescribed by Von Lenk, the gun-cotton would be as perfectly purified as it is by being washed only for a short time and then boiled for a few minutes in an alkaline solution.

If it were possible to operate on a large scale upon *pure* cotton fibre, the functions of the alkaline bath, used as a purifying agent, would simply be to neutralize and remove from the pyroxylin any traces of acid not separated by washing. But as it is only possible to submit cotton to very partial purification in manufacturing operations, its treatment with the acid must partially, or completely, convert into oxidized products the small quantities of resinous and other foreign substances still retained by the tubular fibre. An examination of many specimens of gun-cotton has shown that, at any rate, some of these products, which may be comparatively unstable in character, are much less readily removable from the gun-cotton by simple washing than the acids with which it is impregnated; the solvent action of the alkaline bath upon these is therefore very probably one of its most important functions.

As the difficulties attending the perfect removal of the acid with which gun-cotton remains impregnated after its conver-

sion are mainly attributable to the tubular structure of the cotton fibre, and to the circumstance that the latter contracts considerably upon conversion into pyroxylin, the complete purification of the material is very greatly facilitated by reducing the gun-cotton fibre to a fine state of division, similar to that of the pulp used in paper manufacture, in which form it appears likely that gun-cotton will receive advantageous application. By submission to the "pulping" process, the gun-cotton is divided into very minute fragments, and is at the same time violently agitated for some considerable time with a very large volume of water (rendered slightly alkaline if necessary), which is afterwards thoroughly expressed when the pulp is converted into cylinders or other forms; so that a more searching supplementary process of purification can scarcely be conceived than this disintegration of the gun-cotton.

The treatment of the purified gun-cotton with a solution of soluble glass, which constituted a prominent feature in Von Lenk's system of manufacture when the latter first became known in this country, has been shown by Schrötter, Redtenbacher, and Schneider, by myself, and more recently by Pélouze and Maury, to possess no important merits. If gun-cotton, thus treated, has been found to resist the destructive effects of exposure to elevated temperatures longer than equally pure gun-cotton to which no silicate has been applied, this must be ascribed to the introduction between the fibres of the gun-cotton of small quantities of substances which would exert a neutralizing action upon minute traces of acid not removed from the gun-cotton by the purifying process, or of any acid liberated or generated by the influence of heat.

Some hydrated calcic and magnesian silicates, produced by the decomposition of the alkaline silicate when the gun-cotton is washed in spring-water after its impregnation with soluble glass and desiccation, and possibly some small proportion of alkaline carbonate and silicates, which have escaped removal in the final washing, may exist in the gun-cotton submitted to the silicating treatment, and may act to some extent as protectives, in the manner pointed out. But products of manufacture to which no soluble glass has been applied, but which have remained for many days immersed in somewhat hard water, contain calcic and magnesian carbonates, in proportions

sufficient to exert quite as great a protective action as the substances deposited in the gun-cotton by submission to Von Lenk's "silicating" treatment. In the account of the action of light and heat upon gun-cotton, it will be shown that the impregnation of the material with small proportions of alkaline or earthy carbonates is likely to prove a very important protective measure; but it need hardly be stated that there are much more simple and certain methods of distributing such substances uniformly through a mass of gun-cotton than the treatment with soluble glass and subsequent washing. Thus, considerable quantities of gun-cotton have been uniformly impregnated at Waltham Abbey, for experimental purposes, with sodic carbonate (in the proportions of 0·5 and 1 per cent.), simply by soaking the finished gun-cotton in solutions of that substance, of definite strength, expressing the excess of liquid in the usual manner, and then drying the skeins.

It will be seen from the foregoing observations on the Austrian system of manufacture, that Von Lenk has not actually initiated any new principle as applied to the production of gun-cotton, but that he has so perfected the process of converting cotton-wool into the most explosive form of gun-cotton and of purifying the product, as to render a simple attention to clear and definite regulations alone necessary to ensure the manufacture of a very uniform material, much more perfect in its nature than the products obtained in the earlier days of the history of gun-cotton. Such being the case, too much stress cannot be laid upon the fact that deviations from the prescribed process, which at first sight may appear very trivial, are certain to lead to variations in the products of manufacture, affecting their explosive characters, or their permanence, or both. In discussing the composition of gun-cotton manufactured by Lenk's system, I shall have to refer to several samples of the material, produced at Hirtenberg and at Stowmarket, which differed widely in their composition and properties from the normal product of manufacture. I have obtained conclusive proof that these exceptional variations are solely ascribable to the neglect of a uniformly strict adherence to the prescribed process of converting the cotton; and I am strongly of opinion that their occurrence has almost always been due to the employment of nitric acid which exhibited a fictitious specific gravity, from the presence either of considerable quan-

tities of peroxide of nitrogen, or of some other impurity (such as sulphuric acid). A searching examination of the ordinary products of manufacture obtained at Waltham Abbey, where the quality of the nitric acid employed received uniformly strict attention, has shown that, without any exception, the variations in their composition were embraced within very narrow limits.

II.—Composition of Gun-cotton.

The researches instituted by me into the composition of gun-cotton have been conducted partly with ordinary products of manufacture, obtained from Waltham Abbey and from the gun-cotton factories at Hirtenberg and Stowmarket, and partly with products prepared in the laboratory with purified and very finely carded cotton-wool. The latter was more particularly employed in experiments instituted for the purpose of accurately ascertaining the maximum increase of weight which cotton-wool will sustain by treatment with mixed nitric and sulphuric acids, while the products of ordinary manufacture have been employed in the analytical experiments.

The loosely spun cotton-wool from which these products are obtained varies somewhat in purity, even after the preliminary treatment with alkali and washing which it undergoes previous to conversion. The material, as supplied to Waltham Abbey by the cotton-spinners, always contains seed fragments, which are only very partially removed by the purifying process, but are in most instances completely dissolved or mechanically removed during the processes of conversion and purification. The purified cotton is always considerably inferior in whiteness to the converted material. The loss sustained by the cotton in the treatment with potassic carbonate and subsequent washing, ranged between 5 and 10 per cent. An average sample of the cotton used was submitted to analysis after having been purified in the usual manner. It contained 0·044 per cent. of ash, and the following percentage proportions of carbon and hydrogen:—

	Found.	Cellulose.
Carbon.....	44·26	44·44
Hydrogen	6·05	6·17
Oxygen	49·69	49·39

Hygroscopic Moisture existing in Gun-cotton.—The amount of water absorbed and retained by gun-cotton under normal atmospheric conditions is very uniform; the average proportion is 2 per cent.; and although gun-cotton will gradually absorb as much as 6 per cent. of water if exposed for a sufficient period to a very moist confined atmosphere, the proportion which it retains upon re-exposure to open air rarely exceeds 2 per cent. This amount is rapidly re-absorbed by gun-cotton, after perfect desiccation *in vacuo* over sulphuric acid.

Mineral Constituents of Gun-cotton.—The proportion of mineral constituents (or ash) in gun-cotton has been carefully determined in a large number of products of manufacture. The mode of operation consisted in thoroughly moistening the dried and weighed gun-cotton (about 4 grms.) in distilled water, and then projecting it, in small fragments, into a deep platinum vessel of known weight heated to low redness. The decomposition of the gun-cotton under these conditions is so gradual, that there is no risk of the mechanical dispersion of any of the ash. After the combustion of the gun-cotton was completed, the temperature of the vessel was raised sufficiently to burn off minute quantities of carbon which had separated during the slow combustion. The variation in the amount of ash obtained from different samples of gun-cotton manufactured at the same works was but slight; 1 per cent. was the average proportion existing in gun-cotton manufactured at Waltham Abbey. A few samples examined contained a somewhat higher proportion, and some specimens, obtained from Hirtenberg, furnished an average proportion of nearly 2 per cent. An analysis of the ash in these instances indicated that the gun-cotton had been submitted to the "silicating" treatment adopted by Lenk. The ash furnished by gun-cotton not thus treated consisted principally of calcic carbonate and other impurities (sand, clay, &c.) deposited between the fibres during the immersion of the gun-cotton in the stream.

Proportion of the Gun-cotton Dissolved by Ether and Alcohol.—Hadow found that the highest product which he obtained by the action of nitric and sulphuric acids upon cotton-wool, and the composition of which agreed closely with the requirements of the formula

$$C_6H_7O_5, 3NO_2, \text{ or } C_{12}H_{14}O_7, 3N_2O_5.$$

was perfectly insoluble in any mixture of ether and alcohol; but that the lower products, obtained by the action of acid-mixtures containing larger proportions of water, were more or less readily soluble in ether, used alone or in admixture with alcohol. Although, in operating upon small quantities of carefully purified cotton-wool with a considerable proportion of the acid-mixture, the most explosive gun-cotton can be obtained without difficulty in an almost pure condition, by one single treatment, it could scarcely be expected that, in a manufacturing operation, more than a close approximation to this result could be arrived at, when it is remembered that a considerable time elapses before the action of the acids upon the entire quantity of cotton with which they remain in contact is completed; moreover, during the period occupied by the conversion of the last portions of cotton, the acid in contact with the fibres becomes diluted by the water eliminated in the reaction, and does not therefore retain to the last the composition required for the production of the most explosive gun-cotton. But it is remarkable how very close and uniform an approximation to complete conversion of the cotton into the most explosive product is attained by properly carrying out Von Lenk's instructions.

A very large number of the ordinary products from Waltham Abbey have been carefully examined, with the view of determining the average percentage of soluble matter in the gun-cotton. In the first experiments the weighed gun-cotton (between 2 and 3 grms.) was packed closely into a small tube constricted to a fine opening at the lower extremity. The mixture of ether and alcohol which was poured on to the gun-cotton in the tube filtered through it very slowly. When the filtrate furnished an unimportant quantity of residue, the cotton in the tube was dried and its loss in weight determined. Upon examining the samples of gun-cotton thus treated, they were found, however, still to contain matter soluble in the ethereal mixture, and it was evident that, by this mode of treatment, either the soluble matter could not be separated from the insoluble fibre, or only the most readily soluble portions (which furnish a tolerably limpid solution) were carried through by the liquid; while those less easily dissolved, and which were, indeed, more glutenized than actually dissolved, remained in the tube. A different mode of operating was therefore resorted to. From 8

to 10 grammes of the gun-cotton were digested with the ethereal mixture in a stoppered bottle for from thirty to fifty hours (according to the apparent extent of action of the solvent). The contents of the bottle were then agitated slightly, and a small portion of the gun-cotton was removed and placed as a plug in the apex of a funnel, through which the liquid was filtered into an evaporating dish. The gun-cotton was afterwards carefully expressed over the funnel, again digested for a second (and sometimes a third) similar period with fresh solvent, and finally washed upon the funnel. The liquid thus obtained never contained more than two or three minute fibres of the gun-cotton; it was generally of a very pale straw colour, and slightly opalescent. When evaporated nearly to dryness it became gelatinous, and gradually dried to a yellowish substance of somewhat resinous appearance.

The mean percentage of matter soluble in alcohol and ether, as furnished by the results of examination of twenty samples of ordinary products of manufacture at Waltham Abbey was 2·03, the extreme results obtained were 1·3 and 2·6 per cent.

Somewhat higher results were obtained by submitting the material to long-continued agitation with ether and alcohol, and repeating the digestion and agitation several times with fresh solvent; but the gun-cotton became so disintegrated by this treatment, that it was very difficult to filter the liquid so as to obtain it free from fibres; it was moreover found that a considerable proportion of the finely-divided mineral matter attached to the gun-cotton became suspended in the liquid and could not be separated. Repeated experiments showed that, after the second digestion of Waltham Abbey gun-cotton, there were only very small quantities of soluble matter extracted, which it appeared almost impossible to remove perfectly.

The products of the Waltham Abbey manufacture were submitted to a particularly searching examination, with reference to the proportion of matters extractable by ether and alcohol, because several samples of gun-cotton obtained from the Stowmarket and Hirtenberg factories, furnished results differing considerably from each other and from those obtained with the first Waltham Abbey samples examined.

Thus the proportions of soluble matter found in 15 samples of gun-cotton manufactured at Stowmarket in 1864, ranged

between 3·2 and 12·55 per cent., and no two samples contained the same proportion.

Several products of more recent date obtained from Stowmarket, have, however, furnished much more uniform results, the majority of which correspond nearly to those obtained with the Waltham Abbey gun-cotton.

The soluble matter in nine specimens of gun-cotton obtained from Hirtenberg ranged from 3 to 14 per cent., and one specimen contained so high a proportion that the yarn was entirely broken up by a brief digestion with the solvent; a large quantity of nearly transparent solution was separated from it, but the proportion of gun-cotton remaining insoluble could not be determined with any accuracy. A few other specimens of Hirtenberg gun-cotton corresponded closely with the Waltham Abbey products, as regards the proportion of soluble matter they contained.

The character of the soluble matter extracted from the Waltham Abbey products by ether and alcohol was very uniform.

The dry extracted matter, when digested with hot alcohol alone, dissolved to a considerable extent, and a light yellow solution was obtained, which, on evaporation, furnished a yellow amorphous residue, almost entirely soluble in ammonia or sodic carbonate; the neutral liquids furnished precipitates with lead- and silver-solutions. When the substance was heated with potassic hydrate, ammonia was evolved. When gradually exposed to heat on platinum or bibulous paper, it first fused and then deflagrated. The portion insoluble in alcohol dissolved in the ethereal mixture, the solution yielding on evaporation a semi-opaque film, which contracted and split up into small horny particles when quite dry. The extracts from Stowmarket and Hirtenberg gun-cotton contained the same product soluble in alcohol alone, and generally in about the same proportion; but in most of those instances in which the specimen had furnished a considerable proportion of soluble matter, the part insoluble in alcohol yielded by solution in ether and alcohol, a liquid which approached in its character to photographic collodion, the film left by its evaporation being more or less tough, and nearly transparent. In two instances very good photographs were obtained with the collodion extracted from specimens of Austrian gun-cotton.

The proportions of matter soluble in alcohol alone, and in the ethereal mixture, were successively determined in a few samples of gun-cotton, and furnished the following results:—

Description of gun cotton.	Alcoholic extract. Per cent.	Ethereal extract. Per cent.	Total soluble matter.	Result obtained by direct extraction with ether and alcohol. Per cent.
Waltham Abbey, 1863 ..	0·75	1·31 =	2·06	1·91
„ 1864 ..	0·72	1·35 =	2·07	1·93
„ „ ..	0·95	1·48 =	2·43	2·21
„ „ ..	0·90	1·42 =	2·32	2·60
Stowmarket „ ..	0·78	1·18 =	2·96	3·00
„ „ ..	0·95	11·78 =	12·73	12·55

The foregoing results show that, in the general products of manufacture obtained by properly following Von Lenk's instructions with regard to the conversion of the cotton, the proportion extracted by alcohol alone is somewhat below 1 per cent., and consists of nitrogenized matter, of acid character, which has evidently been produced by the action of nitric acid upon the resinous or foreign substances contained in the cotton at the time of its conversion. The portion soluble in ether and alcohol, but insoluble in spirit, varies in amount between 1 and 2 per cent., and consists of the very small proportion of gun-cotton which has escaped conversion into the most explosive product. The occurrence, in a few quite exceptional instances, of comparatively large proportions of soluble gun-cotton, of the kind produced by the action of a warm somewhat dilute acid mixture upon cotton, affords important evidence of the necessity for adhering strictly to the mode of treatment, and the precautions, which considerable experience and a careful examination of products have proved to be indispensable to the attainment of uniform results in the manufacture of gun-cotton.

With regard to the matter soluble in ether and alcohol found to exist in gun-cotton, the following observations possess some interest, as bearing upon the cause of its production in the manufacture of the substance.

1. The mean proportion of soluble matter furnished by the very concordant results of examination of gun-cotton manufactured at Waltham Abbey in 1863, in the preparation of which the acids, left in contact with the gun-cotton, were in the pro-

portion of 18 parts by weight to 1 of cotton, is 1·62 per cent.; while the mean proportion furnished by the results of examination of sixteen samples of Waltham Abbey products, in the manufacture of which only 10 parts of the acids were left in contact with the gun-cotton, is 2·13 per cent. All the results obtained with the first gun-cotton were below 2 per cent., while out of sixteen results, obtained with the last, eleven were above 2 per cent. Here we have a decided indication that the prolonged contact with acid has some influence upon the composition of the product; the employment of the higher proportion of acid furnished results more nearly approaching perfection than those when the gun-cotton was left in contact with a smaller proportion of the acid mixture. As far as can be judged at present, however, from the general properties of the products the difference observed when the larger or the smaller proportion of acid is used, is not of sufficient importance to render necessary the consumption of the larger quantity of acid in the manufacture.

2. The following experiment was instituted with a portion of one of the specimens of gun-cotton from Stowmarket, which had been found to contain 11·5 per cent. of matter soluble in ether and alcohol (after removal of the portion soluble in alcohol only). The gun-cotton, having been perfectly dried and carefully weighed, was digested for three hours with mixed nitric and sulphuric acids, of the kind always employed. It was afterwards submitted to long-continued washing with distilled water, precautions being taken to prevent mechanical loss. The dry gun-cotton was found to have increased in weight 0·3 per cent. But the original gun-cotton contained 1·71 per cent. of mineral matter, while, after having been digested with acids and washed, it furnished only 1·01 per cent. of ash. The difference between these numbers had therefore to be added to the increase in weight which the gun-cotton sustained by this second treatment with acids, which consequently amounted to 1 per cent. The substance now no longer contained any appreciable amount of soluble matter. Assuming that the soluble gun-cotton originally existing in the sample was either one of those whose composition has been determined by Hadow,

$$(C_{18}H_{22}O_{15}, 8NO_2, \text{ or } C_{18}H_{23}O_{15}, 7NO_2,)$$

the increase sustained by the imperfect sample, if completely

converted into the most explosive and insoluble product, should have amounted in the one instance to 0·61 per cent., and in the other to 1·29 per cent. Considering that neither of these substances would be likely to exist alone in the imperfectly converted material, the actual increase of 1 per cent., sustained by the gun-cotton, must be regarded as a close approximation to the theoretical proportion of imperfectly converted gun-cotton, and proves decisively that, on the one hand, the treatment of the cotton with the acids had not in the first instance been quite perfect, while on the other a further digestion of imperfectly converted gun-cotton with acids will convert soluble gun-cotton, which it contains, into the most explosive or insoluble variety.

Determination of the Carbon, Hydrogen, and Nitrogen contained in Gun-cotton.—The difficulties which attend the application of the ordinary analytical methods to determining the composition of so highly explosive a substance as pyroxylin, need scarcely be dwelt upon. Several special methods of proceeding have been pointed out by different experimenters, and others have been elaborated in the course of these researches; but even the most simple and perfect require great care and some experience in their employment, for the attainment of trustworthy results. The following is a brief account of the most successful methods tried for determining the carbon, hydrogen, and nitrogen, and of the results which each has furnished.

In the majority of instances the specimens of gun-cotton analysed were ordinary products of manufacture. The material operated upon was always purified, as far as possible, by repeated digestion and washing, from matter soluble in ether and alcohol, and, in calculating the results, allowance was made for the mineral constituents of the gun-cotton operated upon.

Carbon Determinations.—Method I.—The gun-cotton yarn was cut into small pieces and dried, and the fragments were introduced singly into a very long combustion-tube, each portion being separated from the next by about 5 centimetres of oxide of copper. When the tube had received the entire quantity to be burned, about 15 centimetres of the anterior portion were filled with oxide of copper, and the remainder (about 20 centimetres) with porous fragments of reduced copper. The potassa-apparatus, used for absorbing carbonic acid, had a small chloride-of-calcium tube attached to it, which was weighed, together

with the apparatus, before and after the combustion. Although the greatest care was taken to proceed as slowly as possible with the heating of those portions of the tube containing the gun-cotton, the successful completion of the operation was a matter of great uncertainty, as the explosive combustion of some small portion of the gun-cotton would very frequently throw the surrounding oxide of copper forward, thus closing the necessary passage in the front part of the tube. This method was therefore abandoned after about two dozen experiments had been made, of which only four were brought to a satisfactory termination.

The results obtained in four experiments by this method ranged from 23·71 to 24·26 per cent., the mean being 24·02 per cent.

Method II.—The weighed substance was saturated with distilled water, and the latter removed as far as possible by pressure. The moist yarn was then cut into eight or ten pieces and introduced separately into one end of a long combustion-tube, open at both extremities, and divided in the centre by a plug of asbestos. The shorter portion of the tube contained only the fragments of gun-cotton placed at distances of about 12 millimetres from each other; the longer portion was previously filled with long layers of oxide of copper, oxidized copper turnings, and porous reduced copper. This part of the tube was connected with a desiccating apparatus, to which were attached the potassa-bulbs with the small weighed chloride-of-calcium tube, fixed on to the outer limb. The extremity of that part of the combustion-tube which contained the gun-cotton was connected with an arrangement for passing an easily regulated current of pure dry air through the apparatus. The two portions of the tube were separated in the furnace by a screen. When the front part of the tube had been raised to a full red heat (at which it was maintained throughout the operation), the pieces of gun-cotton were consecutively made to undergo slow combustion, the portion nearest the asbestos plug being first heated, and the resulting gases and aqueous vapours being carried forward by the slow current of air continuously passed through the apparatus. This passage of air served to oxidize minute portions of carbon separated from the gun-cotton, when the whole tube was raised to a red heat at the close of the operation. The proportion of reduced copper employed was so

regulated, that a considerable quantity remained unoxidized at the conclusion of the experiment. Great care was required in the application of heat to the parts of the tube containing the moist gun-cotton, there being otherwise considerable risk of its fracture by the water expelled from the heated substance.

The results of eight carbon determinations made by this method in different specimens of gun-cotton manufactured in 1863, ranged from 24·11 to 24·66 per cent., the mean being 24·42 per cent.

Method III.—A weighed quantity of gun-cotton, moistened as in the preceding experiments, was placed in a capacious strong Bohemian glass tube, sealed at one end; a small quantity of oxide of copper was introduced into the tube just in front of the gun-cotton. The other extremity of the tube was now constricted, and was sealed when the air had been exhausted. Heat was then carefully applied to the sealed tube until the gun-cotton had undergone slow combustion, and the oxide of copper was afterwards shaken to that part of the tube where a minute carbonaceous deposit had been left by the gun-cotton. The tube was placed in a gas-furnace and connected at one end with an apparatus for delivering pure air and oxygen, and at the other with a long combustion-tube, in a separate furnace, containing layers of oxide of copper and porous reduced copper, to which were attached a large chloride-of-calcium tube and the potassa-apparatus. The two Bohemian tubes were connected by a narrow india-rubber tube, about 12 centimetres long, fitted with a screw clamp, so that communication between the tubes could be cut off or gradually increased. The long tube having been raised to a red heat, the point of the sealed tube which was enclosed in the caoutchouc connexion was broken, and the confined gases were allowed to pass gradually over the heated oxide of copper and metal. When no further escape of gas from the tube took place, the other extremity, connected with the apparatus for delivering air, was broken, and the whole of the products of decomposition of the gun-cotton were gradually conveyed into the heated tube. Pure oxygen was finally passed through the apparatus, and the tube in which the gun-cotton had been burned was heated to redness.

The gun-cotton for these experiments was taken from various products of Waltham Abbey manufacture obtained in 1863 and

1864; the quantity employed varied between 0·2257 grm. and 0·39 grm. The proportions of carbon obtained in nine experiments ranged from 23·85 to 24·6 per cent., the mean being 24·15 per cent.

Method IV.—The gun-cotton was reduced, by cutting, to an extremely fine state of division, and mixed when dry as intimately as possible with a very large proportion of chromate of lead, in the first few experiments, and of finely-divided oxide of copper in the remainder. Long layers of oxide of copper and porous reduced copper were employed as usual, and at the close of the combustion a current of pure oxygen, and finally pure air, was passed through the tube. With care and some experience, the combustion of the substance was brought perfectly under control by this comparatively simple method of proceeding; in a few instances, however, the operation was terminated prematurely by the stopping up of the tube, in consequence of the explosive combustion of a small accumulation of the finely-divided gun-cotton.

The results of 28 carbon determinations in different samples by this method ranged from 24·04 to 24·88, the mean being 24·57 per cent.

The several mean results arrived at by the four different methods employed, are 24·02, 24·42, 24·15, and 24·57; the mean of 49 carbon-determinations is therefore 24·29. But the results, upon the accuracy of which the most perfect reliance is to be placed, are unquestionably those furnished by the fourth method, which gave 24·57 as the mean percentage.

Determination of Hydrogen.—The hydrogen was determined at the same time as the carbon, by the method of operating last described. The results of eight consecutive combustions, conducted with different samples of gun-cotton yarn, were so remarkably uniform, that they were regarded as furnishing ample numerical data with respect to this constituent element. The proportions of hydrogen found ranged between 2·41 and 2·56 per cent., the mean being 2·46 per cent.

Determination of Nitrogen.—The method of Dumas was employed for determining, by volume, the proportion of nitrogen contained in gun-cotton. A rather wide combustion-tube, about 82 centimetres long, was drawn out at one end, so as to admit of being connected with a carbonic acid apparatus provided with a regulating tap; and was fitted at the other end with the

usual form of delivery-tube. 5 centimetres of the tube were first filled with coarse porous fragments of oxide of copper, a layer of 3 centimetres of fine oxide of copper followed, and then the very finely-cut gun-cotton, mixed with a large proportion of oxide of copper; the mixture occupying about 25 centimetres of the tube. The next 22 centimetres were filled partly with coarse porous oxide of copper, and partly with finely powdered oxide; a layer of 20 centimetres of reduced copper followed, and finally, the tube was plugged with coarse porous oxide, occupying a length of about 5 centimetres. The combustion was conducted very slowly, with the usual precautions, pure carbonic acid being passed through the apparatus for the requisite period before commencing, and at the conclusion. The gas collected was found, in one instance only, to contain traces of nitric oxide, and this determination was consequently rejected. The quantity of substance operated upon varied between 0·3006 grm. and 0·415 grm. The percentage proportions of nitrogen, calculated from the corrected volumes of gas observed, ranged between 13·36 and 14·6, in eighteen experiments, the mean being 13·83.

Deductions from the Analytical Results.—The formula adopted by Hadow, as representing the most explosive product of the action of mixed nitric and sulphuric acids upon cellulose,—which is the same as that first suggested for gun-cotton by W. Crum, afterwards adopted as probable by Gerhardt, and recently supported by Schrötter, Redtenbacher, and Schneider,—demands the following percentage proportions of its constituent elements:—

$$C_6H_7N_3O_{11} = C_6 \left\{ \begin{matrix} H_7 \\ 3NO_2 \end{matrix} \right\} O_5.$$

Carbon	72	24·24
Hydrogen	7	2·36
Nitrogen.....	42	14·14
Oxygen	176	59·26
	297	100·00

The formula recently adopted by Pélouze and Maury, as agreeing closely with the results which they obtained in their experiments, requires the following numerical proportions:—

$$C_{24}H_{18}O_{18}, 5NO_5, \text{ or } C_{24}H_{36}O_{18}, 5N_2O_5.$$

Carbon	288	25·00
Hydrogen	36	3·13
Nitrogen.....	140	12·15
Oxygen	688	59·72
	1152	100·00

The following statement shows the relation which the extreme and mean results, obtained in the numerous analytical examinations of gun-cotton manufactured at Waltham Abbey, bear to the two above formulæ :—

Trinitro- or trinitric cellulose.		Results of analysis. Extremes.		Means.	Formula of Pélouze and Maury.
Carbon ..	24·24	23·71	24·26	24·02	25·00
		24·11	24·59	24·42	
		24·06	24·60	24·15	
		24·21	24·78	24·57	
Hydrogen	2·36	2·40	2·47	2·46	3·13
Nitrogen .	14·14	13·36	14·60	13·83	12·15
Oxygen..	59.26				59·72

In comparing the experimental results with the requirements of the two different formulæ, it is necessary to bear in mind the following circumstances :—

1. The gun-cotton examined has not been obtained from *pure* cellulose (for the production of which the most elaborate system of purification has been proved to be necessary), but has been prepared from cotton separated from foreign matters as far as it is possible by the ordinary method of purification adopted.

2. Ample proof has been furnished, by most extensive and rigorous experiments, of the invariable existence in the purified gun-cotton (as produced by the most complete action of the strongest acids upon cotton-wool, purified by treatment with alkali and washing) of notable proportions of substances which owe their existence to the presence of foreign matters remaining in the cotton fibre after its ordinary purification, and also of products resulting from the less perfect action of nitric acid upon small portions of the cellulose.

3. Although these two varieties of impurities were extracted as far as possible by repeated digestion and washing with ether and alcohol, from the pyroxylin analysed, their perfect removal

from the fibre, by the application of any feasible method of purification, is extremely difficult, if not impossible.

4. The existence of even small proportions of these impurities in a sample of pyroxylin will have the effect of raising somewhat the percentage of carbon obtained by analysis of the substance, above that which would be furnished by the pure material, and consequently, also, of reducing to a trifling extent the proportion of nitrogen obtained below the theoretical requirement.

A proof of this is furnished by the analytical results obtained with specimens of the matter soluble in ether and alcohol, which had been extracted from Waltham Abbey gun-cotton.

These results are as follows:—

	Carbon.	Hydrogen.	Nitrogen.
Specimen 1	30·50	2·91	
Specimen 2	29·18 29·28		11·85
Mean results furnished by the gun-cotton after digestion with ether and alcohol	24·15	2·46	13·83

It is believed that the foregoing circumstances must be admitted to account perfectly for the slight variations exhibited, among themselves, by the numerous analytical results which have been quoted. The whole of the carbon-percentages obtained by the most trustworthy method of analysis (Method IV.) are somewhat higher, and the great majority of the results of the nitrogen determinations are a little lower than required by the formula

$$C_6\left\{\begin{matrix}H_7\\3NO_2\end{matrix}\right\}O_5, \text{ or } C_{12}H_{14}O_7, 3N_2O_5.$$

On the other hand, making even very full allowance for errors of analysis, and assuming for an instant the possibility that the substance analysed could be an absolutely pure product, the individual as well as the mean results of the carbon, hydrogen, and nitrogen determinations, are far more closely in accordance with those theoretical requirements than with the percentage results which should be furnished by a pure substance having the composition more recently assigned to pyroxylin by Pélouze and Maury, viz.,

$$C_{24}H_{36}O_{18}, 5N_2O_5.$$

The analytical results of gun-cotton manufactured at Waltham Abbey according to Von Lenk's directions confirm, therefore, the correctness of the conclusions that the most explosive known variety of gun-cotton is *trinitro-cellulose* or *trinitric cellulose;* and that cotton-wool is converted into this substance by the complete action upon it, in the cold, of the mixture of one part by weight of nitric acid of specific gravity 1·52, and three parts of sulphuric acid of specific gravity 1·84.

In addition to the data furnished by the analytical experiments described in the foregoing, others, bearing upon the composition of gun-cotton, have been furnished by different systems of experimental inquiry.

The relation between the nitrogen and carbonic acid obtained by oxidation of gun-cotton has been determined. For this purpose Liebig's method of operating was adopted in the first instance, the gun-cotton being prepared and arranged for combustion as in the case of the nitrogen determinations, and the mixed gases collected in successive proportions and examined.* A few experiments rendered it evident, however, that this method, when applied to the examination of gun-cotton, did not furnish trustworthy results. In the decomposition of this substance, when distributed through a very large proportion of oxide of copper, the oxidation of the carbon does not proceed uniformly; small portions of that element evidently escape oxidation in the first instance, and are only subsequently burned when the nitrogen has already been in great proportion liberated. The proportion which the carbonic acid bears to the nitrogen in the gases successively collected varies therefore frequently as the combustion proceeds; and it would consequently be necessary to collect the entire quantity of gases furnished by the gun-cotton operated upon, in order to arrive at a correct result.

The following statement of the relative proportions by volume of the gases collected successively in two operations of this kind, will serve to illustrate the variable composition of the gas collected at successive stages of one and the same operation. In both experiments the gas had been allowed to escape for

* This method of examination appears, from the description given in their report, to have been the one adopted by Pélouze and Maury in their determinations of the relative proportions of carbonic acid and nitrogen furnished by gun-cotton.

some time, before the first collection, for expulsion of the air in the combustion-tube.

Experiment I.	Carbonic acid.	Nitrogen.
1st tube.	80	20
2nd „	78·75	21·25
3rd „	79·29	20·71
4th „	79·15	20·85
5th „	83·42	16·58

Experiment II.	Carbonic acid.	Nitrogen.
1st tube.	77·45	22·55
2nd „	79·76	20·24
3rd „	79·45	20·55
4th „	79·83	20·17
5th „	78·56	21·44
6th „	77·06	22·94

The majority of results obtained in each of the above experiments are concordant among themselves, and agree closely with the percentage proportions (by volume) of carbonic acid and nitrogen which should be furnished by trinitro-cellulose (namely 80 of carbonic acid to 20 of nitrogen). But in each experiment somewhat discordant results were obtained, and therefore this method of determining the relation between the carbon and nitrogen in gun-cotton was abandoned as not sufficiently trustworthy. It should be observed, however, that even the mean of the several results obtained in each experiment corresponds much more closely with the volume-proportion which should be furnished by trinitro-cellulose, than with that demanded by the formula which Pélouze and Maury adopt, as the following comparison shows:—

	Theory.		Experiment.	
	$C_{24}H_{36}O_{18}5N_2O_5$	$C_6H_7O_23NO_2$	I.	II.
Nitrogen.....	17·2	20	21·28	19·88

Several determinations of the relative proportions of carbonic acid and nitrogen have been made by Bunsen's method. The mode of operating was as follows: into a very stout wide Bohemian glass tube, about 22 centimetres long and sealed at one end, were introduced, first some reduced copper, then about 0·1 to 0·15 grm. of the dry gun-cotton, and afterwards sufficient oxide to fill about 4 centimetres of the tube. The open extremity of the latter was constricted, and sealed when air had been exhausted. The gun-cotton was then decomposed by applying the flame of a lamp for a short time to the tube. After the oxide of copper had been distributed over the surface

of the tube (to the interior of which it adhered, in consequence of the deposition of water from the exploded gun-cotton upon the glass), the latter was introduced into a vessel of wrought iron, within which it was compactly surrounded on all sides by very fine sand. The vessel consisted simply of a piece of gas-pipe about 25 centimetres long and of 3 centimetres internal diameter, closed at one end by means of a plug welded into it, and provided at the other extremity with a screw-cap. A few small perforations were drilled into the sides of the pipe. The glass tube was exposed in this envelope to a red heat for about one hour; when cold, it was opened under mercury, and the gas transferred and examined in the usual manner. The results thus arrived at, which will be quoted presently, were very concordant, and stood in close relation to the results obtained by the separate determinations of carbon and nitrogen in gun-cotton.

The reproduction of cotton from pyroxylin by Hadow's method has been made the subject of many experiments, with the view of controlling by its means the analytical and synthetical results obtained. It was found that by submitting purified insoluble gun-cotton to the action of an alcoholic solution of potassic sulphhydrate, as directed by Hadow, the amount of cotton obtained corresponded closely with the theoretical proportion to be furnished by trinitro-cellulose.

The following results may be quoted as examples. They were obtained with gun-cotton which contained only small proportions of matter soluble in ether and alcohol. From 4·064 grms. to 4·898 grms. of substance were employed.

Description of gun-cotton.	Cotton obtained.	Cotton to be obtained by trinitro-cellulose.
Austrian, coarse yarn.....	55·24 per cent.	
„ „ „	55·08 „	
Waltham Abbey, coarse....	55·38 „	
„ „ fine.....	55·30 „	
Laboratory products, No. 1.	54·22 „	54·54 per cent.
„ „ No. 2.	54·48 „	
„ „ No. 3.	54·85 „	
„ „ No. 4.	54·16 „	
„ „ No. 5.	53·64 „	

In conducting experiments on this method of examination, a

liability to mechanical loss was observed when a very strong solution of the potassic sulphhydrate was employed, in consequence of the fibre becoming to a considerable extent disintegrated during the digestion; but this can be easily avoided by employing the reagent in a more dilute form. The solution best adapted for effecting the complete reduction of gun-cotton by digestion in the cold, without breaking up the fibre, was obtained by preparing a saturated solution of potassic hydrate, completely saturating this with sulphhydric acid, and diluting the liquid thus obtained with half its volume of alcohol.

A small loss of product occurs generally, even when the sulphhydrate-solution is not stronger than just described, in consequence of a feeble solvent action exerted by the liquid upon the *reduced* cotton.* In one experiment a sample of cotton obtained from gun-cotton sustained a loss of 0·6 per cent. on digestion in the cold for forty-eight hours with the sulphhydrate.

A slight excess (about 0·5 per cent.) is sometimes exhibited by the weight of the reduced cotton over the amount which should be furnished, theoretically, by pure trinitro-cellulose. The cause of this was very carefully examined into, and proved to be mainly due to the presence in the specimen examined of a proportion of material resulting from the less perfect action of nitric acid upon some portions of the cotton fibre. Unfortunately, however, the fluctuations in the results which may be furnished by different examinations of the same specimen of gun-cotton by this method, though they might be regarded as not very important in an ordinary analytical process, may be equivalent to differences which would be caused by very considerable variation in the amount of soluble gun-cotton present in the substance.

The proportions of cotton which should be furnished by pure trinitro-cellulose, and by the lower products which Hadow has examined, are as follows:—

		Cotton.
$C_6H_7O_5$, $3NO_2$, or $C_{18}H_{21}O_{15}$, $9NO_2$	furnishes	54·54 per cent.
Compound B .... $C_{18}H_{22}O_{15}$, $8NO_2$	„	57·45 „
Compound C†.... $C_{18}H_{23}O_{15}$, $7NO_2$	„	60·67 „

* Cotton, in the original form of carded wool, is not dissolved by the potassic sulphhydrate.

† A product possessing the properties of compound C, described by Hadow, and

Supposing that the matter soluble in ether and alcohol in a specimen of gun-cotton amounted to 2 per cent., and consisted of the compound C, the result of the analysis should be affected by that impurity to the extent of about 0·1 per cent. An excess of 0·5 per cent. obtained in the examination of a sample should therefore indicate the existence of 10 per cent. of compound C (readily soluble gun-cotton) in the sample; or if the specimen contained that percentage of compound B, this would only affect the result by 0·3 per cent. It cannot be confidently asserted that the errors of the method itself are ever less than from 0·3 to 0·5 per cent.

It is evident, therefore, that this method of examining gun-cotton, though useful as a mode of controlling the results obtained by determining the increase of weight which cotton sustains by treatment with nitric acid, under varied circumstances, is not susceptible of affording sufficiently definite and trustworthy results to render it applicable as a method of ascertaining the degree of freedom from soluble gun-cotton, of products of manufacture.

Experiments on the increase sustained by Cotton in its conversion into Gun-cotton.—Hadow found that cotton-wool, by treatment with the strongest mixture of nitric and sulphuric acids, sustained an increase of 81·34 per cent., that the gun-cotton produced was quite insoluble in mixtures of ether and alcohol, and that the increase of weight which cellulose should sustain

agreeing closely in its composition with the requirements of the formula assigned to that body, has been manufactured in considerable quantities at Waltham Abbey, for experimental purposes, by submitting cotton-yarn to digestion for the customary period with an acid-mixture which differed from that employed in the manufacture of insoluble gun-cotton, in containing $3H_2O$ in addition.

The substance possessed feeble explosive properties, was readily soluble in ether and in glacial acetic acid, with the exception of a small proportion of foreign matter, which rendered the solution slightly turbid. The results obtained by determinations of carbon and nitrogen in the substance corresponded very closely to the proportions which should be furnished by $C_{18}H_{23}O_{15}, 7NO_2$, as the following comparison shows:

		Theory.		Experiment.		
Carbon.....	18 =	216 =	26·97	27·08	27·01	27·17
Nitrogen	7 =	98 =	12·23	12·42	12·41	
Hydrogen.....	23 =	23 =	2·87			
Oxygen.....	29 =	464 =	57·93			
		801	100·00			

by conversion into the trinitro-cellulose agreed very nearly with the results of his experiment.

Pélouze's earlier experiments fixed the *maximum* increase in weight sustained by cotton upon conversion into gun-cotton at 76 per cent. But in the recent report of Pélouze and Maury it is stated that, in a number of laboratory experiments in which the composition of the acid-mixture, the proportions borne by the acid used to the cotton treated, and the duration of the treatment, were variously modified, the increase in weight of the cotton fluctuated within narrow limits, and did not exceed 78 per cent. The authors are led, mainly by these results, to adopt the formula

$$C_{24}H_{36}O_{18}, 5N_2O_5,$$

because cellulose, by conversion into a substance having the percentage-composition which that formula demands, should sustain an increase of weight of 77·78; a number which is very slightly *below* the maximum result obtained in their experiments.

It should be stated that they describe the acids employed by them in all their experiments as follows: the sulphuric acid had a density of 66° Baumé (which corresponds to a specific gravity of 1·767), and the nitric acid had a specific gravity of 1·50 at 9° C.

It will be observed that these acids, but more especially the sulphuric acid, are very notably inferior in strength to those prescribed by Von Lenk, which have been used in all the experiments now described, and are always employed in the manufacture of gun-cotton at Waltham Abbey; namely, sulphuric acid of specific gravity 1·833 to 1·84 (somewhat above 69° Baumé), and nitric acid of specific gravity 1·52 at 15° C. It appears most probable, from many of the experimental observations included in these researches, that such discrepancies as exist between the results arrived at by Pélouze and Maury, and by Hadow, the German chemists and myself, are to be mainly ascribed to the differences in the strength of acids employed.

The subjoined results of very numerous experiments will, I believe, be admitted not only to establish satisfactorily the correctness of Hadow's statement, that cotton-wool may be made to sustain an increase in weight above 81 per cent., but also to

show that the results of other experimenters who have found the increase sustained by cotton not to exceed 78 per cent., are in perfect harmony with the conclusion that the product of the complete action, upon cotton-wool, of certain mixtures of the strongest nitric and sulphuric acids, *is the substance* $C_6H_7N_3O_{11}$, *in a nearly pure condition.*

The following statement shows the increase of weight which finely carded cotton-wool of very high quality, previously purified by treatment with alkali and washing, has sustained by single and successive digestions, for different periods, with the prescribed acid-mixture. The products were always purified by careful washing with distilled water.

No. of Experiments.	Quantity of cotton operated upon.	Proportion of acid to cotton.	Duration of treatment.	Temperature of acid used.	Increase in weight on 100 of cotton.
1	3·704 grms. submitted to six successive treatments.	From 60 to 70 parts of acid to 1 part of cotton.	1st treatment, 1 hour. 2nd treatment, 3·5 hours. 3rd treatment, 18 „ 4th treatment, 18 „ 5th treatment, 48 „ 6th treatment, 48 „	15° C. „ „ „ „ „	79·40 79·96 80·26 82·13 81·28 80·26
2	3·087 grms.	50 to 1	48 hours.	„	81·86
3	1·132 grm.	„	24 „	„	82·57
4	1·263 „	„	24 „	„	82·04
5	1·083 „	14·6 to 1	24 „	„	80·07
6	3·222 grms.	10 to 1	48 „	„	78·79
7	1·907 grm.	10 to 1	12 „	„	78·13
8	2·468 grms.	50 to 1	10 minutes.	„	62·43
9	1·668 grm.	50 to 1	15 „	55° C.	78·98

Experiment 1 shows that a repeated immersion of the gun-cotton in a fresh mixture of the acids raised the weight of 100 parts of cotton to 182·13, a number somewhat higher than that obtained by Hadow; but that, by protracting the treatment beyond the point when the product ceased to increase in weight, a slight but continuous loss was sustained, which, there appears no doubt, from the results of confirmatory experiments, is to be ascribed to the solution of small quantities of gun-cotton in the strong acids with which it was left in prolonged contact.

The following results show that the *repeated* immersion of cotton in an acid-mixture of somewhat less strength, does not effect, nearly as rapidly or as completely, its conversion into in-

soluble gun-cotton, as does a single treatment with the acid-mixture prescribed by Von Lenk.

(*Experiment* 10.)—2·12 grms. of pure dry cotton were submitted to two successive treatments with a cold mixture of acids having the composition

$$\left.\begin{matrix}HNO_3\\H_2SO_4\end{matrix}\right\} + 3H_2O.*$$

Period of first immersion three hours, increase in weight ..... 62·34 per cent.
Period of second immersion nine hours, increase in weight ..... 65·14 per cent.

The product was then digested for three hours in the cold with the strongest acid-mixture, after which the total increase in weight was 77·51 per cent.

Experiments 2, 3, and 4 prove that, by a single treatment of cotton with a considerable proportion of the strongest acid-mixture, results may be obtained closely in accordance with the number given by Hadow, and with the theoretical requirement of trinitro-cellulose. The mean of these three experiments fixes the maximum increase in weight which cotton is capable of attaining by this treatment at 82·16 per cent.; the theoretical number is 83·3 per cent.

Experiments 5, 6, and 7 show that, even in operating upon small quantities of comparatively very pure cotton, if the proportions of the acid-mixture used be limited to such as are employed in manufacturing operations (10 to 14 parts to 1 of cotton), the conversion into trinitro-cellulose cannot be as completely accomplished. In these instances, the increase of weight sustained by the cotton is between 78 and 80 per cent. As might have been anticipated, the products contained notable proportions of matter soluble in ether and alcohol, while those obtained in experiments 2, 3, and 4 yielded a minute trace to the solvent.

Experiment 8 demonstrates the importance of continuing the digestion with acids longer than is merely necessary for the production of an explosive material, if it is desired to effect as complete a conversion as possible into insoluble gun-cotton.

* This is the composition of the mixture which Hadow believes to be the weakest which is capable of producing insoluble gun-cotton by repeated immersions. The nearest expression of the composition of Von Lenk's acid-mixture is $\left\{\begin{matrix}10HNO_3.\\19H_2SO_4.\end{matrix}\right.$

By immersion for ten minutes only, the cotton increased in weight only 62·43 per cent., and the product was to a considerable extent soluble in ether and alcohol. In another experiment, a still more soluble product was obtained by immersion for only three minutes. Experiments 6 and 7 indicate that, the quantity of acid used being limited, digestion for twelve hours is scarcely sufficient to ensure the maximum attainable increase of weight; and the results of experiments 3 and 4, compared with those of 1 and 2, indicate that under equal conditions, the result obtained by immersion for twenty-four hours is quite equal to that furnished by more protracted digestion. This observation is fully borne out by the results of manufacturing operations, as pointed out in the first part of this memoir. There is no doubt that an actual loss of product, though only slight, is sustained by prolonging the contact of the acids with the gun-cotton much beyond the period necessary for its perfect production.

Experiment 9 shows that a very brief treatment of cotton with a warm acid-mixture effects its conversion into insoluble gun-cotton as completely as a long-continued treatment with cold acids (the proportion of the latter being limited). This experiment was made for the purpose of ascertaining whether, with the employment of the strongest acids, heat exerted a similar influence upon the character of the product to what it does when weaker acid-mixtures, or mixtures of saltpetre and sulphuric acid are employed. This is evidently not the case, for the product obtained was as slightly soluble as the general products of manufacture at Waltham Abbey. It was also found that a few minutes' immersion in a warm acid-mixture converted an imperfect product, obtained by a few minutes' treatment with *cold* acids and containing much soluble matter, into a gun-cotton of the ordinary kind.

The following results were obtained by submitting samples of cotton-yarn (taken from ordinary supplies for the manufacture of gun-cotton) to treatment with the usual mixture of acids, the cotton having previously been boiled in an alkaline-bath and washed: after which treatment it still retained a very few fragments of seed.

Experiment.	Cotton employed.	Duration of immersion.	Increase in weight. on 100 parts of cotton.
11	4·777 grms.	48 hours	78·43
12	8·076 „	48 „	78·19
13	6·0206 „	24 „	80·77
14	6·901 „	24 „	80·79
15	9·2147 „	48 „	78·14

In all these experiments a considerable excess of acids (about 60 parts to 1 of cotton) was employed. They afford decided evidence of the influence which the quality of the cotton employed must exert upon the quantity of product obtained even in a laboratory operation; and show that the results furnished, under most favourable circumstances, by cotton of ordinary commercial quality, fluctuate between 78 and 81 per cent., never quite reaching the latter number. The results also point, as did some of those obtained with the purer cotton, to a tendency of the gun-cotton to dissolve in the acid-mixture when the immersion is continued for a very long period. Both results (experiments 13 and 14) obtained by treatment of the cotton for twenty-four hours are notably higher than those furnished by the forty-eight hours' treatment. The loss of product ascribable to this cause is doubtless somewhat greater in these experiments than in manufacturing operations, where the proportion of acid to the cotton used is considerably lower.*

A comparison of the weight of cotton obtained from samples of gun-cotton, with the original weight of cotton employed in their production, affords data which are strongly in support of the conclusion that the differences between the increase in weight which cotton should sustain by conversion into trinitrocellulose, $C_6H_7N_3O_{11}$, and the results furnished by as perfect a treatment of different specimens of cotton as is practicable, are to be ascribed, not merely to the presence, in the products,

* Upon reconversion into gun-cotton of some specimens of the reduced cotton, which is always in a friable condition very favourable to solution, the weights of the resulting products indicated that a more considerable proportion of the gun-cotton produced was dissolved than when the original cotton was operated upon.

One sample sustained an increase of weight of only 73·91 per cent., and a second 73 per cent. by immersion for the usual period. A third sample, submitted to a brief treatment, gave an increase of 77·61 per cent., and upon being immersed a second time for twenty-four hours, the weight of the product indicated an increase of only 75·15 per cent.

of small quantities of imperfectly converted soluble gun-cotton, but also to the existence in them of substances which are foreign to the cotton, and which are only partially removable by simple washing with water.

The following are the results of very careful experiments made with finely-carded and specially purified cotton-wool, and with ordinary cotton-yarn, purified by boiling with potassic carbonate. The increase sustained by the cotton upon its conversion into gun-cotton having been noted, the product was reconverted into cotton by Hadow's method, special care being taken to avoid mechanical loss in the several operations. The weights of the cotton recovered compared with those of the original cotton, and with the increase of weight sustained by the latter when converted into gun-cotton, are as follows:—

Description of cotton.	Proportion of acids to cotton.	Increase sustained by conversion.	Cotton employed.	Cotton recovered.	Loss upon the original cotton.
		Per cent.	grms.	grms.	Per cent.
Finely carded and purified.	50 to 1	82·57	1·132	1·119	1·14
Ditto	Ditto	82·04	1·263	1·2526	0·83
Ditto	14·6 to 1	80·07	1·083	1·0695	1·24
Cotton yarn, ordinary quality.	60 and 70 to 1	78·43	4·777	4·574	4·43
Ditto		78·19	8·076	7·561	6·34
Ditto		80·77	6·0206	5·6862	5·55
Ditto		80·79	6·901	6·5319	5·36

It will be seen from the above statement, that the cotton which was recovered from the laboratory products, furnished by comparatively very pure cotton which had sustained an increase of weight of 82 and 82·6 per cent. (the theoretical increase being 83·3 per cent.), amounted to only about 1 per cent. less than the cotton originally taken; and that when the employment of a limited quantity of acid (as in the third experiment) yielded a product the weight of which represented about 2 per cent. less increase than these, the cotton recovered was in this instance also only about 1 per cent. below the quantity employed, the difference in the weight of the nitro-product having been due only to the formation of a somewhat larger proportion of soluble gun-cotton. It appears from these results, and estimating the proportion of loss which the processes of conversion and reduction may involve at about 0·5

per cent., that the particular cotton-wool operated upon contained about 0·5 per cent. of matter foreign to cellulose, which was eliminated in the course of the transformation and reproduction of the latter. But, when less pure samples of cotton were converted as completely as practicable into insoluble gun-cotton, and furnished results from 1·75 to 4 per cent. lower than those obtained by similar treatment of the pure material, the weight of the recovered cotton indicated a loss upon the original substance employed of from 4·4 to 6·3 per cent., an increased loss which must be due to the larger proportion of foreign matters existing in the cotton operated upon. These facts surely afford strong support to the conclusion that the deficiency in weight exhibited by the products obtained from ordinary cotton-wool, even after its purification with alkali, as compared with those furnished under the same circumstances by purer cotton-wool, is due to the presence of foreign matters in the cotton, which, though partially retained by the gun-cotton, exist there in the form of products whose formation does not add, in so high a proportion, to the original weight of the cotton as does the production of trinitro-cellulose.

It follows from the above results, obtained by treatment of the ordinary cotton-wool with a considerable excess of acid, that if the same cotton be treated with the limited proportion of acid-mixture (10 to 14 parts by weight to 1 part of cotton) employed in the ordinary course of manufacture, the products must then exhibit somewhat less increase of weight (lower proportions, therefore, than 178 or 180 from 100 of cotton), because, under those circumstances, the production of larger proportions of the lower cellulose-products (soluble in ether and alcohol) comes into play to cause a reduction in the weight of the product beyond that which is ascribable mainly to the influence of the foreign matters in the cotton.

Two quantitative operations have been conducted in the ordinary course of manufacture at Waltham Abbey, with the view of ascertaining the actual quantity of gun-cotton furnished by 100 parts of cotton in the ordinary course of operating with considerable quantities of material.

In one experiment the cotton employed, which contained about the average quantity of seed, and had as usual the peculiar colour of unbleached fibre, was submitted to the ordinary purification in the bath of potassic carbonate, and was

dried as usual for twenty-four hours at 50° C. before immersion in acids. Its weight, when dry, was 31 lbs. 6 oz. It was afterwards treated in all respects like an ordinary product of manufacture. The weight of the air-dry gun-cotton showed an increase upon the original dry cotton of 74·3 upon 100 parts. The weight of the thoroughly dry product corresponded to an increase of 71 upon 100.

In another experiment, made with a somewhat higher quality of cotton, an increase of 76 per cent. was obtained.

The products of these operations were quite similar in character to those usually obtained, and to the results furnished by the laboratory-experiments just now described, which were conducted with samples of the same description of cotton. A difference of about 9 per cent. between the latter results and the lowest number furnished by the quantitative manufacturing experiments has therefore to be accounted for. The following statements will show that this deficiency is not greater than would be anticipated.

In the cotton operated upon, besides the resinous and other impurities which are partly removed by solution in the acid and by subsequent extraction in the purifying processes, and which also occasion a notable loss in the laboratory-experiments with this kind of cotton, as already pointed out, there exists a more or less considerable proportion of seed, of which only minute particles are here and there observed in the finished gun-cotton. To this source of loss upon the weight of the cotton employed, has to be added the mechanical loss of product unavoidably attending the repeated submission of the gun-cotton to the expressing and long-continued washing processes. But the principal loss of product, and one which alone suffices to account for the difference observed between the results of the laboratory-experiments and those of ordinary manufacturing operations, occurs in boiling the gun-cotton in the alkaline-bath. The brief digestion of the material in the weak solution of potassic carbonate not only abstracts a considerable proportion of the products foreign to gun-cotton, resulting from the action of the acids upon the impurities which the cotton fibre obstinately retains, but also causes a very notable proportion of the gun-cotton itself to pass into solution.

A quantity of Waltham Abbey gun-cotton which had, in the ordinary course, already been submitted to the treatment with

alkali, was boiled for ten minutes in a solution of potassic carbonate precisely similar to that usually employed (of spec. grav. 1·02). The liquid became of an amber colour, and the gun-cotton, when dried, was found to have sustained a loss of 3·7 per cent. The same gun-cotton was again boiled for twenty minutes in the same alkaline-bath, which deepened in colour considerably during this second employment. The total loss sustained by the material, after this second treatment, amounted to 12·09 per cent.*

9·22 grms. of cotton-yarn, previously purified by treatment with alkali and carefully freed from seed, were converted into gun-cotton in the ordinary manner, excepting that about three times the ordinary proportion of acid was used, whereby the solution of foreign matters in the acid was promoted. The product, after long-continued washing in distilled water, was dried and weighed. The increase sustained by the cotton amounted to 78·14 per cent. (a number closely corresponding to the laboratory-results previously described). The gun-cotton was then boiled for eleven minutes in a solution of potassic carbonate of the usual strength. When washed and again dried, it was found to have lost considerably in weight, and the finished product showed an increase of weight upon the original cotton equivalent to 69·8 upon 100, which was therefore 1·2 per cent. less than the lowest result obtained in the manufacturing operations. It is easily conceivable that, in the smaller operations, the gun-cotton, though submitted only for exactly the usual period to treatment with an alkaline-bath of the ordinary strength, should sustain a somewhat greater loss than a large compact mass of the material, such as is always operated upon. But the results of these experiments establish a source of loss in the usual process of manufacture, which fully accounts for the discrepancies exhibited between the yields of usual manufacturing operations and of laboratory operations conducted with the same description of cotton, in which the treatment with boiling alkaline water has been omitted.

* The treatment of gun-cotton with a boiling solution of potassic carbonate of the prescribed strength, even if greatly prolonged, does not affect the composition of the mass, but evidently acts by dissolving, and transforming into other products, portions of the fibre, or of its surfaces. The combustion of a specimen of ordinary gun-cotton which had been boiled for one hour in the alkaline bath furnished 24·48 per cent. of carbon (the theoretical number of trinitro-cellulose being 24·24 per cent.).

Comparison between Analytical and Synthetical Results.—The relative proportions of carbonic acid and nitrogen furnished by the complete oxidation of gun-cotton, afford the means of instituting a comparison between the analytical and synthetical results, of which the details have been given, and, it is believed of demonstrating beyond dispute the correctness of the conclusion, that the product of the complete action upon cotton-wool of the mixture of strongest acids prescribed by Von Lenk is most correctly represented by the formula

$$C_6H_7N_3O_{11},$$

of which the expression

$$C_6H_7O_5, 3NO_2$$

appears to be the most rational interpretation. The method of determining the relative proportions of the two gases furnished by gun-cotton has been already described. The following results were furnished by four samples of gun-cotton :—

	Volume proportions of carbonic acid and nitrogen.		Proportions required by
	I.	II.	$C_6H_7N_3O_{11}$.
Carbonic acid	62·25 = 81·22	76·899 = 80·91	80
Nitrogen....	14·40 = 18·78	18·144 = 19·09	20
	III.	IV.*	$C_{24}H_{36}O_{18}5N_2O_5$.
Carbonic acid	83·64 = 80·91	72·397 = 80·91	82·8
Nitrogen....	19·73 = 19·09	17·082 = 19·09	17·2

The proportion of nitrogen furnished by the first experiment, though somewhat low, is nearer to the requirements of the trinitro-cellulose formula than to those of the formula adopted by Pélouze and Maury. The proportions of the gases observed in the other three experiments, which happen to be identical in their results, correspond with the requirements of $C_6H_7N_3O_{11}$ as closely as could possibly be expected when operating upon a substance of approximate purity only.

* A sample of gun-cotton which had been left in contact with acids for five days, and a second sample, which had been twice submitted to the ordinary treatment with acids, furnished the following results :—

	5 days in acid.	Twice dipped.	Trinitro-cellulose.
Carbonic acid	80·574	80·37	80
Nitrogen	19·426	19·63	20

Upon calculating the proportion which the nitrogen found in these experiments bears to the mean percentage of carbon (24·6) obtained by the most trustworthy method employed for the determination of that element, the following numbers are obtained:—

	I.	II, III, & IV.
Carbon.....	24·6	24·6
Nitrogen	13·32	13·59

These percentage-proportions of nitrogen are not only in perfect accordance with a considerable number of the results obtained by direct determination of the volume of nitrogen furnished by samples of Waltham Abbey gun-cotton; they are also as close approximations to the theoretical percentage of nitrogen in trinitro-cellulose as the analysis of products containing small proportions of lower nitro-compounds could be expected to furnish; and lastly, the increase in weight which cotton of average purity should sustain by conversion into nitro-cellulose-products which furnish these proportions of nitrogen, corresponds closely to the average results obtained by operating upon moderately pure cotton with the mixed acids of *prescribed strength* and in the proportion (about 10 parts to 1 of cotton) indicated by Von Lenk.

The general conclusions to be deduced from the experimental results described in this memoir are as follows:—

1. The products obtained by submitting cotton-wool to treatment with the prescribed mixture of nitric and sulphuric acids, and to purification as directed by Von Lenk, are very uniform in character; they consist almost entirely of the most explosive known variety of gun-cotton or pyroxylin, which is insoluble in mixtures of ether and alcohol. This substance, when produced upon a manufacturing scale, contains from 1 to 2 per cent. of mineral substances, and a small proportion, varying with the quality of the cotton, of matters soluble in alcohol, partaking of acid properties, and consisting chiefly, if not entirely, of products of the action of nitric acid upon resinous or other bodies enclosed in the cotton fibre. There is also always present in the gun-cotton a small quantity (from 1 to 3 per cent.) of cellulose products of a less explosive character, soluble in mixtures of ether and alcohol, which result from the incomplete action of nitric acid upon small portions of the cotton operated upon

2. The gun cotton, when purified as far as it is possible from foreign substances, soluble in alcohol and in ether and alcohol, furnishes analytical results which agree much more closely with those demanded by the formula

$$C_6H_7N_3O_{11}, \text{ or } C_6H_7O_5, 3NO_2,$$

than with the requirements of the formula $C_{24}H_{36}O_{18},5N_2O_5$, recently adopted for gun-cotton by Pélouze and Maury.

3. If cotton-wool of great purity is digested for a period of about twenty-four hours with a considerable proportion of the prescribed acid-mixture (about 50 parts to one of cotton), it sustains an increase of weight ranging between 81·8 and 82·6 upon 100 of cotton. Lower results (between 78 and 80 per cent. increase) are obtained by digesting the cotton for a short period only, or for very considerable periods, by using a limited proportion of the acid (from 10 to 14 parts to 1 of cotton), by employment of acids of slightly lower specific gravities than those specified, and by operating upon cotton of somewhat lower quality. The digestion, for a second or third time, of products which have exhibited a comparatively low increase of weight, in an acid-mixture of the kind first used, or of greater strength, has the effect of raising the weight of the product to within the higher limits above named.

The increase in weight which 100 parts of pure cellulose should sustain, theoretically, by complete conversion into a substance of the composition $C_6H_7N_3O_{11}$, is 83·3, while if converted into a substance of the formula $C_{24}H_{36}O_{18},5N_2O_5$, the increase sustained by it only amounts to 77·8 upon 100 parts.

4. Cotton-wool always contains, even after careful purification, small proportions of foreign organic substances, the presence of which, in the material submitted to treatment with the acids, must affect to some extent the quantity of the product obtained.

5. It is extremely difficult, indeed apparently impossible, even in operating under most favourable conditions upon small quantities of cotton-wool, to convert this substance *completely* into the highest nitric product—the perfectly insoluble gun-cotton. Small quantities of gun-cotton soluble in ether and alcohol can always be extracted from the products; the quantities are only minute in the highest laboratory-products, but they are always very appreciable in the most perfect manufacturing products.

Their invariable formation must unquestionably cause the increase of weight sustained by cotton to be somewhat less than that which theory would demand.

6. The long-continued digestion of the gun-cotton in the acid-mixture, the several mechanical operations to which it is submitted in the course of its purification, and above all, the solvent action exerted not only upon certain bye-products, but also upon the gun-cotton itself by the alkaline liquid, in which it is boiled for a short time, are all sources of loss which, in examining into the results of a system of manufacture, must not be disregarded, and the existence of which explains satisfactorily the difference observed between the weights of laboratory-products and those of manufacturing operations.

7. In accepting the formula proposed by Pélouze and Maury for gun-cotton, it would be necessary to assume that the cotton-wool operated upon was pure cellulose; that the operation of conversion was an absolutely perfect chemical process; that there were no possible sources of loss in the production of the material; and that in all laboratory operations which had furnished an increase of weight above the theoretical demand (77·8 per cent.), some substance, differing in composition from the ordinary products of manufacture, must have been obtained.

8. The identity in their characters, and close resemblance in composition, of the most perfect products of laboratory operations and of the *purified* products of manufacture, the very close approximation in the weight of the former to the theoretical demands of the formula

$$C_6H_7N_3O_{11}$$

(which may be expressed as

$$C_6H_7O_5, 3NO_2, \text{ or } C_{12}H_{14}O_7, 3N_2O_5),$$

and the satisfactory manner in which the unavoidable production of somewhat lower results in the manufacturing operations admits of practical demonstration, appear to afford conclusive evidence of the correctness of either of those formulæ as representing the composition of the most explosive gun-cotton, and to demonstrate satisfactorily that the material, prepared strictly according to the directions perfected by Von Lenk, consists uniformly of that substance (now generally known as *trinitro-cellulose*) in a nearly pure condition.

XXXII.—*On the Constitution of Phosphites.*

By C. Rammelsberg.

Sir H. Davy, in 1812, discovered phosphorous acid, formed by the action of trichloride of phosphorus on water; Dulong in 1816, described the crystallised acid; and Berzelius,* in 1818, showed, by analysis of the salts of barium and lead, that the oxygen-ratio of the base and the acid in phosphites is 2 to 3. The celebrated Swedish chemist found at once, that these salts contain water, which cannot be expelled by heat without decomposition of the acid; in phosphite of lead the oxygen of the basis and water was as 2 to 1, in phosphite of barium as 1 to 1. Ten years later, H. Rose published† his investigations on phosphites, particularly concerning their behaviour at high temperatures. His analyses confirmed the result of Berzelius, on the composition of earthy and metallic phosphites, and the presence of chemically combined water, necessary for their constitution, which is decomposed by heat, its oxygen forming phosphoric acid, and its hydrogen being evolved in the gaseous state. H. Rose confirmed, moreover, the differences in the amount of water in phosphites; 2 atoms were found in the salts of barium, strontium, and calcium; 1 atom only in the salts of lead, manganese, and zinc. In the course of his investigations on phosphoretted hydrogen, H. Rose pointed out, that the salts of hypophosphorous acid likewise include chemically combined water (2 atoms).

In the years 1842 and 1843, two important papers on these acids, were published by A. Wurtz,‡ in Paris, containing a great number of analyses of hypophosphites, and of some phosphites and organic derivatives of phosphorous acid. Wurtz adopted the view that phosphites and hypophosphites contain no water, but are salts of acids the radical of which includes hydrogen.

If we adopt the modern atomic weights (H=1,C=16,P=31)

* Afhandlingar i Fisik, iv (Schw. Journ. xxiii, 153).

† Poggendorff's Annalen, ix, 23, 215.
Ann. Ch. Pharm. xliii, 318; lviii, 49.

we may now say, that Wurtz established for crystallised phosphorous acid the formula H_3PO_3, and for the phosphites, the formulæ—

$$HR'_2PO_3 \text{ and } HR''PO_3.$$

He therefore asserts, *that all salts of phosphorous acid contain only the elements of one atom of water* (expressed in the old way), while the experiments of Berzelius and H. Rose had proved that certain phosphites include the elements of *two* atoms of water. One of the most important is phosphite of barium, $2BaO.PO_3 + 2HO$; Wurtz says that his own analyses of this salt agree with those of H. Rose; but he assigns to it the formula $2BaO.PHO_4 + HO = HBaPO_3 + \frac{1}{2}H_2O$,* and maintains that $\frac{1}{2}H_2O$ is water of crystallisation, and is expelled at 150—200°. Every one will comprehend that he assumes the contrary of the facts proved by two eminent chemists.

The question on the true constitution of phosphites and phosphorous acid requires new investigations, to decide, whether there really exist two series of salts,

$$HR''PO_3 = H_2R''_2P_2O_6$$

and

$$H_4R''_2P_2O_7,$$

and, before all, whether the last may be changed into the first by the loss of H_2O. Such was the purpose of my experiments, briefly described in the sequel.

Phosphite of Barium.

A solution of trichloride of phosphorus in water, mixed with chloride of barium, gives a precipitate when ammonia is added.

Phosphite of barium, after drying in the air, gives off a small quantity of water when heated to 200—250°.

Berzelius found.....	Ba = 61·25	per cent.
H. Rose „	Ba = 60·18	„
Mean of eight determinations =	60·89	„

Several determinations of phosphorus were also made, to make sure that the atomic relation Ba : P is 1 : 1.

All these results confirm the formula—

$$H_4Ba_2P_2O_7.$$

* Ba = 137.

		Calculated.
4 H	= 4	0·89
2 Ba	= 274	60·62
2 P	= 62	13·72
7 O	= 112	24·77
	452	100·00

The same results are obtained when the phosphite is prepared by a fresh solution of crystallised acid H_3PO_3.

Wurtz ascribes to the phosphite of barium the formula—

$$PHO_4.2BaO.2HO,$$

or—

$$2HBaPO_3 + aq.$$

2 H	= 2	0·46	2	
2 Ba	= 274	63·13	274	
2 P	= 62	14·29	62	
6 O	= 96	22·12	96	
	434	100·00	aq. 18	= 4·0 p.c.
			452	

But the salt gives off only 1·5—1·7 per cent. of water, and the dry salt contains less of barium and phosphorus than is here supposed.

It is well known, that a phosphite treated with nitric acid, is changed into a phosphate, *i. e.*, a pyrophosphate, the quantity of which affords also a verification of the formula, because a salt $H_4R_4P_7$ must give the same quantity of pyrophosphate minus the amount of the hydrogen, while a salt $HRPO_3$ or $H_2R_2P_2O_6$, by changing into $R_2P_2O_7$, assumes O = 16 parts, and loses in the same time only H_2 = 2 parts.

$H_4Ba_2P_2O_7$ = 99·11 per cent. $Ba_2P_2O_7$
$H_2Ba_2P_2O_6$ = 103·2 „ „

Berzelius obtained 97·5 per cent., H. Rose 99·3 per cent., and I have always found, also, nearly 99 per cent.

I have made a singular observation concerning the nature of the product formed by the action of nitric acid on phosphite of barium. When it is treated with hydrochloric acid, only a part dissolves, while another portion remains in red-hot fusion, like a glass, and consists of baric metaphosphate BaP_2O_6.

			Observed.
Ba	= 137	46·44	46·9
2 P	= 62	21·02	20·9
6 O	= 96	32·54	
	295	100·00	

Phosphite of barium is evidently changed by nitric acid into pyrophosphate, metaphosphate, and nitrate; the nitrate becomes, by heating, BaO. In fact, water dissolves BaO, and the whole has the composition of pyrophosphate, because 1 mol. of metaphosphate and 1 molecule of baryta are equal to 1 mol. of pyrophosphate—

$$\begin{array}{l} BaP_2O_6 \\ Ba\ \ O \\ \hline Ba_2P_2O_7 \end{array}$$

The product of oxidation seems to be,—

	Calc.	Observed.
$4\ Ba_2P_2O_7$	= 80·00	
BaO	= 6·83	
BaP_2O_6	= 13·17	12·78
$5\ Ba_2P_2O_7$	100·00	

When phosphite of barium is heated, no trace of water appears; hydrogen is evolved with traces of phosphoretted hydrogen, and the white residue becomes yellow on cooling. My own results agree with those of H. Rose, who has shown, that $H_4Ba_2P_2O_7$ is decomposed into H_4 and pyrophosphate. When the residue is digested with a solution of sulphate of soda, it is easy to precipitate pyrophosphate of silver, the composition of which I have confirmed by analysis.

Phosphite of Strontium.

White crystalline powder, containing 2 molecules of water which are given off at 200°.

$$H_4Sr_2P_2O_7 + 2\ aq.$$

			Observed.
4 H	= 4	1·03	
2 Sr	= 176	45·13	44·53
2 P	= 62	16·00	16·69
7 O	= 112	28·61	
2 aq.	= 36	9·23	10·82
	390	100·00	

The dry salt is decomposed by heat, and gives no water, but hydrogen and pyrophosphate of strontium.

Phosphite of Calcium.

This salt resembles the preceding, and contains also 2 molecules of water (*a*); but when dried at a gentle heat, only 1 molecule (*b*).

	a. $H_4Ca_2P_2O_7+2$ aq.			*b.* $H_4Ca_2P_2O_7+$ aq.		
			Observed.			Observed.
4 H =	4	1·36			1·45	
2 Ca =	80	27·21	27·16		29·00	28·26
2 P =	62	21·09	21·90		22·46	22·22
7 O =	112	38·09			40·57	
2 aq. =	36	12·25	13·23	aq. 18	6·52	6·82
	294	100·00		276	100·00	

The decomposition by heat gives the same products, H_4 and $Ca_2P_2O_7$.

By secondary reaction, small quantities of phosphoretted hydrogen and free phosphorus are formed in all these cases.

Phosphite of Magnesium.

This salt, prepared with solution of trichloride of phosphorus and sulphate of magnesia, or by dissolving the carbonate in pure phosphorous acid, is precipitated, after incomplete neutralization of the liquid with carbonate of soda. H. Rose has already observed, that it is more soluble at common temperatures; its solution must therefore be precipitated by heating or boiling, and the salt washed with hot water.

It contains 1 atom of magnesium to 1 atom of phosphorus,

like the other salts, for the solution in hydrochloric acid mixed with chlorate of potash is entirely precipitated by ammonia. But there are different hydrates.

From dilute liquids the precipitate is wholly crystalline, particularly after longer contact with the solution, and then contains 12 molecules of water, which are expelled at 200°.

$H_4Mg_2P_2O_7 + 12$ aq.

			Observed.		
4 H =	4	0·90			
2 Mg =	48	10·86	10·39	10·69	10·97
2 P =	62	14·03	13·42	13·75	14·17
7 O =	112	25·34			
12 aq. =	216	48·87	50·00	49·77	47·35
	442	100·00			

In dry air, in the desiccator, it gives off 7 molecules of water = 23·5 per cent., and the residue is identical with the salt precipitated by heating its solution:

$H_4Mg_2P_2O_9 + 5$ aq.

			Observed.		
4 H =	4	1·27			
2 Mg =	48	15·19	15·05	15·03	15·37
2 P =	62	19·62	19·44	19·41	19·39
7 O =	112	35·42			
5 aq. =	90	28·50	28·28	28·82	
	316	100·00			

There can be no doubt, that the magnesium-salt of phosphorous acid in the dry state contains H_2 : Mg, for the formula $HMgPO_3$ requires a greater amount both of Mg and of P, and the quantity of pyrophosphate, $Mg_2P_2O_7$, generated by the action of nitric acid, affords another proof of the above assertion. I obtained 96·0, 96·37, 97·06, 97·65, 98·45, 99·7 per cent., while

$$100\ H_4Mg_2P_2O_7 = 98{\cdot}23\ Mg_2P_2O_7$$
$$100\ HMgPO_3 = 106{\cdot}7\ \text{„}$$

Nevertheless, it appears from the results of several analyses, that under certain conditions, another relation between H and Mg may exist. Further experiments are, however, required

to determine these conditions. Meanwhile it may be sufficient to say, that two analyses agree with the formula

$$HMgPO_3 + 4aq;$$

four other products gave—

$$H_3MgPO_4 + xaq.$$

The salt $H_4Mg_2P_2O_7$ does not give off water even when strongly heated, but is decomposed at a red heat into hydrogen and pyrophosphate. Besides these products, certain quantities of phosphoretted hydrogen and free phosphorus appear, and the white residue becomes yellow on cooling.

To illustrate the nature of the residue, I will here describe the results of a single experiment. 100 parts of the dried salt gave 93·68 after ignition. When digested in hydrochloric acid it left a small quantity of red phosphorus, which was determined separately, while the amounts of magnesium and phosphorus in the solution were fixed by other experiments. Thus 100 parts of the residue gave :—

P	1·80	(in the free state).
P	25·74	92·17 $Mg_2P_2O_7$.
Mg	19·93	
O	46·50	
Mg	3·29	5·48 MgO.
O	2·19	
	99·45	

Now 100 parts of

$$H_4Mg_2P_2O_7 = 93{\cdot}68 \text{ residue},$$

contain—

			Containing.	
Mg	21·24		21·74	
P	27·43		24·10	25·78.
		(free)	1·68	

Thence it follows, that only 1·65 parts of the whole quantity (27·43) of phosphorus escape in the gaseous state, or in the form of phosphoretted hydrogen, and I believe that a certain quantity of phosphide of magnesium is formed and afterwards decomposed by atmospheric oxygen.

Ammonia produces, in solutions of phosphite of magnesium, a crystalline precipitate, from which I obtained—

NH_4	4·51			4·80
Mg	9·43	10·2	9·82	10·41
P	17·29		17·74	18·16

The formulæ—

$$\left.\begin{matrix}H_4\\Am_2\end{matrix}\right\}Mg_3P_4O_{12}+16\text{ aq.} \qquad \left.\begin{matrix}H_8\\Am_2\end{matrix}\right\}Mg_3P_4O_{14}+16\text{ aq.}$$

require—

4 H	= 4	0·56	8 H	= 8	1·06
2 Am	= 36	5·03	2 Am	= 36	4·76
3 Mg	= 72	10·06	3 Mg	= 72	9·58
4 P	= 124	17·32	4 P	= 124	16·49
12 O	= 192	26·79	14 O	= 224	29·81
16 aq.	= 288	40·24	16 aq.	= 288	38·30
	716	100·00		752	100·00

It is difficult to say which of these two formulæ should be adopted. The first corresponds to $4H_3PO_3$, the second to $2H_8P_2O_7$.

Phosphite of Nickel.

This salt was prepared by the solution of trichloride of phosphorus, or pure phosphorous acid, carbonate of nickel, and a sufficient quantity of carbonate of soda, taking care that the liquid still remained decidedly acid. A green precipitate is then formed, containing, when dried in the air, a variable quantity of hygroscopic water.

Loss on drying at 250°.	Loss on drying over sulphuric acid.
26·38 per cent.	12·67 per cent.
25·25 „	
26·68 „	12·31 „
24·53 „	
28·52 „	15·84 „
26·27 „	

It must be remarked that the analysis of this and other similar salts is very difficult, because the separation of nickel

(cobalt, zinc, manganese) from phosphorus by ordinary means (hydrosulphates, or fusion with alkaline carbonate), is not perfect. This must be borne in mind in estimating the results of the numerous analyses which I have made on these phosphites.

		Found in the salt dried at 250°.				
Ni	40·60	39·12	40·13	38·17	39·20	38·32
P		20·32	21·46	19·47	20·34	

Hence it is certain, that phosphite of nickel is—

$$H_4Ni_2P_2O_7.$$

			Mean.
4 H	= 4	1·36	
2 Ni	= 116	39·46	39·26
2 P	= 62	21·09	20·40
7 O	= 112	38·09	
	294	100·00	

By oxidation with nitric acid, 100 parts gave—

97·44, 97·60, 98·1, 98·2, 98·98 $Ni_2P_2O_7$,

while calculation affords 98·64 per cent.

My experiments prove, that phosphite of nickel contains 6 molecules of water, $H_4Ni_2P_2O_7 + 6aq$ = 26·86 per cent. of water, half of which goes off over sulphuric acid.

On decomposition by heat, it evolves pure hydrogen and changes into pyrophosphate, mixed with a small quantity of phosphide, which remains on treating the residue with dilute hydrochloric acid.

Phosphite of Cobalt.

This salt is prepared in the same manner, and forms a fine, red precipitate, but becomes blue on drying at 250°.

Loss of water on drying.	Amount of CO and P in the dry salt.	
19·80 per cent.	44·47 per cent.	
	41·31 „	22·43 per cent.
21·08 „	43·28 „	23·03 „
	41·84 „	22·94 „
21·85 „	41·55 „	
	41·79 „	23·74 „
21·12 „	41·58 „	
	43·37 „	22·50 „
20·91 „	43·04 „	

Hence the formula—

		$HCoPO_3$.	
H =	1	0·71	
Co =	60	42·86	$= Co_2P_2O_7 = 105.$
P =	31	22·14	
3 O =	48	34·29	
	140	100·00	

The treatment with nitric acid yielded 102·4 and 103·3 per cent. of the pyrophosphate.

On the contrary, the formula $H_4Co_2P_2O_7$, analogous to that of the nickel-salt, would require only 40·27 Co, 20·8 P, and 98·66 pyrophosphate.

Before drying, the salt evidently contains 2 molecules of water—

$HCoPO_3 + 2$ aq.

	Calculated.	
$HCoPO_3$ =	140	79·54
2 aq. =	36	20·46
	176	100·00

In the desiccator half the water goes off (observed 9·08 per cent.).

According to H. Rose, the cobalt-salt, when decomposed by heat, shows the phenomenon of incandescence, evolves pure hydrogen, and leaves a black residue.

My own experiments confirm these results. The dry salt yielded 97·6—98·9 per cent. of residue = $CoPO_3$, a mixture of pyrophosphate with black phosphide of cobalt, which partly remains when the whole is treated with hydrochloric acid.

This phosphide dissolves in nitric acid, with evolution of red nitrous vapours, and contains, according to an analysis, nearly equal numbers of atoms of cobalt and phosphorus.

The whole residue, converted into pyrophosphate by nitric acid, gave 105 per cent. (calculated 105·7).

I therefore suppose that phosphite of cobalt gives—

$$7\,HCoPO_3 = H_7,\ 3\,\begin{matrix}Co_2P_2O_7\\ Co\ P\end{matrix}$$

$$7\,Co\,P\,O_3$$

Phosphite of Manganese.

For the most part this salt appears as a reddish-white powder, sometimes in coherent pieces of more dark colour.

The analyses prove that the salt, dried as before at 200—250°, corresponds with the formula

$$HMnPO_3.$$

		Calculated.		Observed.			
H	= 1	0·74					
Mn	= 55	40·74	39·7	40·43	40·0	41·7	
P	= 31	22·96	23·2	22·45			
3 O	= 48	35·56					
	135	100·00					

In the air-dried state, it contains 1 molecule of water.

$HMnPO_3$	= 135	88·24		
aq.	= 18	11·76	11·68	12·0
	153	100·00		

When dried over oil of vitriol, it contains two-thirds of this water = 8·16 per cent. (by observation 8·04—8·36).

$HMnPO_3$ should give 105 per cent. $Mn_2P_2O_7$; I have obtained 103.

The formula $H_4Mn_2P_2O_7$ is totally inadmissible, for it would require 38·2 Mn and 98·6 pyrophosphate.

H. Rose, in describing the behaviour of the manganese salt when heated, says that hydrogen, mixed with phosphoretted hydrogen, is, evolved with spontaneous incandescence, and a basic phosphate $Mn_5P_4O_{15}$ is formed; but he determined only

the quantity of manganese in the residue. I found its quantity equal to

98·1 98·76 99·2 per cent.

of the dried salt. If this salt were $MnPO_3$, it should be = 99·26 per cent., containing—

				Observed.	
Mn = 55	41·05	41·27	41·45	42·12	40·96
P = 31	23·13		23·96	23·66	23·23
3 O = 48	35·82				
134	100·00				

Its colour and behaviour to nitric acid indicate the presence of phosphide of manganese, and I believe it to be $3Mn_2P_2O_7$ (pyrophosphate) and MnP, as in the cases before mentioned. The analytical data likewise prove that the loss of phosphorus in the free state, or in combination with hydrogen, is very small.

Phosphite of Zinc.

A fine crystalline powder. After drying over sulphuric acid, it loses only some hygroscopic water, but at 200—250° the loss is nearly 20 per cent.

I obtained the following numbers for the salt in the dry state:—

Zn	43·22	46·27	46·05	45·93	46·07	47·14	45·82	44·05
P		21·80		21·15	20·42	20·16	22·00	

After oxidation by nitric acid:

103·0 102·3 103·4 103·9 103·1

Notwithstanding the considerable differences caused by the great difficulties in separating zinc from phosphorus in the phosphate or pyrophosphate, the composition of phosphite of zinc must be

$HZnPO_3$.

H =	1	0·69	
Zn =	65	44·83	= 104·8 $Zn_2P_2O_7$.
P =	31	21·38	
3 O =	48	33·10	
	145	100·00	

The formula $H_4Zn_2P_2O_7$ would give only 98·7 per cent. of pyrophosphate.

But a still better proof is the existence of the salt $HZnPO_3$ in the anhydrous state, which I have obtained by dissolving the phosphite in free phosphorous acid, and treating the first portion of crystallised salt with water. The product gave, at 250°, only 1·3 per cent. of water. It produced, with nitric acid, 104·8 per cent. of pyrophosphate, and afforded 45·47 per cent. Zn, and 21·53 P.

The hydrated salt contains 2 or 2·5 molecules of water.

$HZnPO_3 + 2$ aq. = 19·0 per cent.
$2HZnPO_3 + 5$ aq. = 23·7 „ of water.

The last agrees with the formula $2ZnO.PO_3.6HO$, assigned to the zinc-salt by H. Rose, who, however, believed it to be

$$2ZnO.PO_3.2HO + 4 \text{ aq.} = H_4Zn_2P_4O_7 + 4 \text{ aq.};$$

this, however, was only a conclusion from the products of its decomposition by heat. We shall see hereafter that such a combination may really exist, and was perhaps examined by Rose; but, considering the numbers afforded by the anhydrous salt, it is impossible that the analyses before cited can relate to $H_4Zn_2P_2O_7 + 4$ aq., isomeric with $2HZnPO_3 + 5$ aq.

The last is decomposed at high temperatures, the evolved hydrogen being sometimes pure, but frequently accompanied by a small portion of phosphoretted hydrogen, while traces of free phosphorus appear. The white residue becomes brown on cooling if atmospheric air enters into the vessel. Its quantity I found = 98—99 per cent. of the phosphite. If $HZnPO_3$ is decomposed into H and $ZnPO_3$, the residue should be = 99·3 per cent.

$ZnPO_3$.

				Observed.
Zn	=	65	45·14	45·81
P	=	31	21·53	21·75
3 O	=	48	33·33	
		144	100·00	

It must be regarded as pyrophosphate and phosphide.

$$3\,Zn_2P_2O_7 + ZnP = 7\,ZnPO_3.$$

Notwithstanding that the zinc salt commonly formed is doubtless $HZnPO_3$, I have analysed a precipitate, apparently formed under the same conditions, which contained 14—15 per cent. of hydrate-water; the same also in the anhydrous state.

			$H_4Zn_2P_2O_7$		
			4 H =	4	1·30
Zn	40·84	41·32	2 Zn =	130	42·20
P	22·64	21·37	2 P =	62	20·13
			7 O =	112	36·37
				308	100·00

$H_4Zn_2P_2O_7 + 3$ aq.

			Observed.	
$H_4Zn_2P_2O_7$	= 308	85·08		
3 aq	= 54	14·92	14·65	14·57
	362	100·00		

It must not be overlooked that such a compound is isomeric with the salt $HZnPO_3 + 2$ aq., the amount of zinc and phosphorus being the same in both, but that of water differing greatly; and I believe that very slight modifications in the conditions of the experiment may give rise to one or the other of them.

Phosphite of Cadmium.

This salt was precipitated from the solution of carbonate of cadmium in that of the trichloride, by addition of a convenient quantity of carbonate of soda. In the dry state it is

$HCdPO_3$

			Observed.	
H =	1	0·52		
Cd =	112	58·33	57·46	57·88
P =	31	16·15	15·49	15·17
3 O =	48	25·00		
	192	100·00		

The precipitate itself is

$3\,HCdPO_3 + 3$ aq.

			Observed.
$2\,HCdPO_3$	= 384	87·67	
3 aq.	= 54	12·33	11·79
	438	100·00	

Half of the water goes off on drying over sulphuric acid.

By heat it is decomposed into hydrogen and a residue = $CdPO_3$; besides which, a trace of phosphorus becomes free, and metallic cadmium is sublimed.

				Observed.
$100\,HCdPO_3$ =	$CdPO_3$		99·48	98·9
	Cd	112	58·6	59·4
	P	31	16·2	14·6
	3 O	48	25·2	
		191	100·0	

Like the other residues, it must be regarded as $3Cd_2P_2O_7$ (pyrophosphate) and $CdP = 7CdPO_3$.

Phosphite of Lead.

It seems unnecessary to confirm the formula $HPbPO_3$, established by the researches of Berzelius and Wurtz. The salt must be prepared with pure phosphorous acid and carbonate of lead, because, if the trichloride is used, it is almost impossible to obtain the salt free from chloride of lead. I give the result of only one analysis:—

	$HPbPO_3$		Observed.	
H =	1	0·35		
Pb =	207	72·12	72·14	(72·04 and 72·31 Berzelius).
P =	31	10·80		
3 O =	48	16·73		
	287	100·00		

After drying over oil of vitriol, the salt gave, at 200°, 2·6—2·8 per cent. of loss, whence I conclude that the precipitated salt contains one-half molecule of water.

$2\,HPbPO_3 + aq.$

$2\,HPbPO_3$ =	574	96·96
aq. =	18	3·04
	592	100.00

According to H. Rose, the products of decomposition of

phosphite of lead are hydrogen, phosphoretted hydrogen, free phosphorus, and a blackish residue = $Pb_5P_4O_{15}$. Hence it would follow that $5HPbPO_3$ give off H_5 and P. I obtained 97·99 per cent., and the residue is, I believe, pyrophosphate mixed with phosphide, to which it owes the colour. That is also the opinion of Wurtz. Phosphorus, both free and combined with hydrogen, is a secondary product of the action of atmospheric oxygen on the phosphide, and that of the hydrogen on the pyrophosphate.

Phosphite of Copper.

By the researches of Wurtz, it is well known that the blue crystalline copper-salt is $HCuPO_3 + 2aq.$, and that at 130° it is for the most part decomposed.

I can only add to these facts that the salt, on drying over sulphuric acid, loses one-fourth of its water, and that it may be boiled with water without decomposition.

Phosphite of Iron (Ferric phosphite).

A dilute solution of trichloride of phosphorus, mixed with a convenient quantity of carbonate of soda, but still acid, is precipitated by iron-alum. The white colour of the compound changes, on drying in the air, into yellowish.

The results of an analysis agree with the formula—

$H_3FeP_3O_9 + 9\,aq.$

			Observed.
3 H	= 3	0·58	
Fe	= 112	21·80	22·19
3 P	= 93	18·09	18·58
9 O	= 144	28·02	
9 aq.	= 162	31·51	30·53
	514	100·00	

I cannot confirm the phenomenon of ignition, or the evolution of phosphoretted hydrogen observed in the decomposition of the salt by H. Rose. It evolved only hydrogen; and in consequence of pyrophosphate of protoxide of iron, formed by the action of the hydrogen, the well-dried salt gave a small quan-

tity of water. The pyrophosphate $Fe_2P_6O_{21}$ is the principal constituent of the residue.

The researches of Berzelius, H. Rose, Wurtz, and my own have proved that phosphorous acid forms two series of normal salts :—

A	B
HK_2PO_3	$H_4Ba_2P_2O_7$
HNa_2PO_3	$H_4Sr_2P_2O_7$
HAm_2PO_3	$H_4Ca_2P_2O_7$
$HCoPO_3$	$H_4Mg_2P_2O_7$
$HMnPO_3$	$H_4Ni_2P_2O_7$
$HZnPO_3$	$[H_4Zn_2P_2O_7]$
$HCdPO_3$	
$HCuPO_3$	
$HPbPO_3$	
H_3FePO_3	
$[HMgPO_3]$	

The hydrogen of these salts cannot be replaced by a metal; they are not acid salts.

In accordance with modern views, it seems necessary to take the hydrogen as a constituent of the acid. But, judging from the facts, either there are two modifications of phosphorous acid,

$$H_3PO_3 \text{ and } H_8P_2O_7,$$

or, it exists only in the first, and the salts B are $2HR''PO_3 + H_2O$, *i.e.*, they contain half of the hydrogen as a constituent element, half as water. That is the opinion of Wurtz.

Now I shall endeavour to show that both these suppositions are inadmissible.

It is well known that the idea of modifications of an acid by the loss or the assimilation of water, or the elements of water, originated from the classic researches of Graham on phosphoric acid, which have greatly contributed to the progress of science. But this idea cannot be adapted to the phosphites, because the same acid gives with nickel the salt $H_4Ni_2P_2O_7$, and with cobalt the salt $HCoPO_3$, and because, for example, the barium-salt $H_4Ba_2P_2O_7$ is precipitated by the solution of PCl_3, as well as by the freshly prepared solution of the crystallised acid H_3PO_3. Moreover, I have obtained two salts of magnesium and of zinc belonging to both series, under nearly the same conditions.

Let us now examine the view of Wurtz, that there is only one class of phosphites, HR'_2PO_3 and $HR''PO_3$, and that the rest consist of 2 molecules of these and 1 molecule of water, $2HRPO_3 . H_2O$.

I have shown that the assertion of Wurtz, that the barium-salt is $2HBaPO_3 . H_2O$, and loses H_2O on drying, is erroneous. All the salts of like composition do not give off water, but only hydrogen on decomposition, like the rest. There is therefore no reason for supposing that half of their hydrogen is in a different form from the rest.

I find it most accordant with the observed facts to assume that all phosphites contain their hydrogen, combined with oxygen, in the form of water,

$$\left\{\begin{matrix} R_2P_2O_5 \\ H_2O \end{matrix}\right. \text{ and } \left\{\begin{matrix} R_2P_2O_5 \\ 2\,H_2O \end{matrix}\right.$$

the water existing in an intimate or intrinsic connection with the molecules of $R_2P_2O_5$.

Many compounds, formerly considered as hydrates, are now more rightly regarded as compounds of hydrogen. We assent to the view that sulphuric acid is not $SO_3 + H_2O$, but H_2SO_4; caustic potash not $K_2O + H_2O$, but HKO; alcohol not $C_4H_{10}O + H_2O$, but $\left.\begin{matrix} H \\ C_2H_5 \end{matrix}\right\}O$, &c.

We imagine the molecules of these substances to be formed in a similar manner to those of water itself, half of the hydrogen being replaced by an elementary or compound radical; and the theory of the hydracids, founded by Dulong and Davy, has acquired an important place in modern chemistry. Instead of water, the elements of water are supposed in numerous cases to enter into compounds.

Such a view is, however, limited by evident facts, and we must confess that true hydrates exist as molecular complexes for the most part of not very intimate connection. Salts often crystallise with different amounts of water, depending upon temperature and concentration. They lose water in dry air, and recover it in moist air. Now it is impossible to believe that water would be decomposed and formed under these conditions. We do not suppose that the temperature is a criterion for the pre-existence of water or not; if the molecules of a compound containing H and O incline to another arrangement,

water may be formed at every degree of temperature, as in the spontaneous and explosive decomposition of chlorate or bromate of ammonia, just as we must suppose a decomposition of water to take place when sulphuric anhydride attracts the atmospheric water, and forms sulphuric acid.

Most salts are stable compounds; all changes produced by temperature leave the essential part of their molecules unaltered, water only being eliminated; and there is no indication that the atomic complexes which determine the peculiar nature of the salts, participate in the decomposition; indeed, many salts form crystals in the anhydrous state, as well as when associated with molecules of water. But when phosphate of soda is heated to 240°, the last molecule of water is driven off, and at the same time the nature of the salt-molecule changes, and cannot be restored by the presence of water. We therefore conclude that the elements of this last molecule of water belong to the atomic complex itself, which is HNa_2PO_4; and in general it is evident that water, appearing under certain circumstances, is formed by combination of its elements.

On the contrary, there are facts which prove that compounds containing water can be decomposed in such a manner that the water is drawn into the movement of the atoms of the molecules; then oxygen or hydrogen will appear, as far as the nature of the active attractions may allow.

Fluoride of potassium and antimony, K_2SbFl_7, crystallises with 2 molecules of water. On exposing it to heat, hydrofluoric acid is formed by the decomposition of water. Peroxide of barium forms a hydrate with 8 molecules of water, and becomes anhydrous when gently heated to 130°; but on heating it rapidly, an explosive decomposition is observed, oxygen becoming free, and hydroxide of barium, H_2BaO_2, being produced. Hence we must conclude that the crystallised compound is not H_2BaO_4 + 7aq., but BaO_2 + 8aq.

The phosphites give no water on decomposition, but only hydrogen; and we suppose that this hydrogen belongs to water, the oxygen of which has been fixed in the new molecules of pyrophosphate.

True phosphorous acid must then be $H_4P_2O_5$, and the crystallised acid, like some of the salts, includes 1 molecule of water, $\begin{cases} H_4P_2O_5 \\ H_2O. \end{cases}$

On examining the crystallised acid, I found it impossible to separate this water, for the crystals melted in a current of hydrogen, and when heated, even with every precaution, soon began to evolve phosphoretted hydrogen. The association between $H_4P_2O_5$, or $R''_2P_2O_5$ and H_2O, or $2H_2O$, is evidently much more intimate than that of water in common hydrates, or the tendency of the former groups to alter the arrangement of their atoms is preponderant; and while the products of trichloride of phosphorus and alcohol, so well described by Wurtz, seem still to include this molecule of water, the triethyl-phosphite of Railton, produced by anhydrous alcohol, may be an analogous compound, in which $(C_2H_5)_2O$ replaces H_2O.

Analogy requires that the hypophosphites shall have a similar constitution. By the researches of H. Rose and Wurtz, we know that they are $H_2R'PO_2$ and $H_4R''P_2O_4$,; that the hydrogen cannot be replaced by metal, and when the salts are decomposed by heat, one-fourth of the hydrogen appears in form of water, three-fourths in the form of phosphoretted hydrogen.

This is the principal difference between the phosphites and hypophosphites, for both acids in the free state give the same products. Solutions of alkaline hypophosphites are transformed, in contact with air, into phosphites, while the acid itself is said to be unalterable; both have a reducing power on the salts of gold, silver, and mercury. We may therefore consider hypophosphites also as containing water in a more intimate connection, like phosphites,

$$\begin{Bmatrix} RPO \\ H_2O \end{Bmatrix} \text{ or } \begin{Bmatrix} R_2P_2O_2 \\ 2H_2O \end{Bmatrix} \text{ and } \begin{Bmatrix} R''P_2O_2 \\ 2H_2O \end{Bmatrix}$$

derived from

$$\begin{Bmatrix} HPO \\ H_2O \end{Bmatrix} \text{ or } \begin{Bmatrix} H_2P_2O_2 \\ 2H_2O. \end{Bmatrix}$$

Although the acid has not yet been obtained in the concrete form, the researches on hypophosphites hitherto made seem to prove that the relation of the equivalents of H and R are the same in all; but it is not impossible that further investigation may give results analogous to those obtained with the phosphites. Moreover, some facts observed with respect to the calcium-salt, by H. Rose, lead me to suppose the existence of

$$H_6R''_2P_4O_7 = \begin{Bmatrix} 2RP_2O_2 \\ 3H_2O, \end{Bmatrix}$$

H. Rose had inferred from his own researches that a difference exists between the two series of phosphites in respect of their decomposition by heat. In his last analytical work (*Traité complet*) he says that the salts $H_4R_2P_2O_7$ give only hydrogen and pyrophosphates, while the salts $HRPO_3$ give $H_3P + H_2$.

My own experiments have led me to the conviction that such a difference does not exist; but that all phosphites give hydrogen and pyrophosphates; and that phosphides, free phosphorus, and phosphoretted hydrogen accompany these bodies in most cases as secondary products.

XXXIII.—*On the Changes in the Proportion of Acid and Sugar present in Grapes, during the Progress of Ripening.*

By A. Dupré, Ph.D.

It is well known that the percentage of free acid present in grape-juice diminishes with the increasing ripeness of the grape, the percentage of sugar increasing at the same time considerably. From this it has frequently been inferred, that in the process of ripening, the acid is transformed into sugar. However, this may be, a little consideration will show that such a conclusion cannot be safely drawn merely from the diminished percentage of free acid, inasmuch as the weight of the fruit augments considerably during the progress of growth; and thus the total amount of free acid present in the ripe fruit may actually be greater than it is in the unripe, and yet its proportion per cent. may be considerably diminished. Moreover, the free acid is not by any means a measure of the total amount of acid present, since there is always some acid united to an alkali, and a greater proportion of alkali in the ripe fruit would account for a diminution of the free acid, even without any increase in the weight of the fruit.

I have not hitherto met with any analytical results giving the requisite data for the above calculation, and I have therefore endeavoured to supply them by the following experiments. The grapes experimented on were selected to correspond as far

as possible with fair average samples of their state of growth. The berries were then cut off the stalks as close as possible to the berry, and the weight of a hundred of them was carefully taken. They were then crushed in a mortar, and the free acid and sugar were either estimated in the total berries, or the skins and kernels were separated, and the acid and sugar estimated in the juice only. In some cases the amount of combined acid was also determined by estimating the amount of carbonate of potassa present in the ash of the juice; and lastly, the amount of tartaric acid was estimated in several samples.

The following tables give the results, showing firstly, the amount of acid, sugar, &c., per cent.; and secondly, the amounts as contained in one hundred berries.

TABLE 1.

Riesling Grapes from Raventhal.

1st. Taken September 13th, 1866:—

Weight of 100 berries		107·60 grms.
consisting of skins.....	11·49	
kernels....	7·95	
juice.....	88·16	
		107·60 „

	The juice contained in 100 parts:—		The juice from 100 berries contained therefore:—	
Sugar.....	2·98	per cent.	2·630	grm.
Acid (calculated as $\bar{T}$ free)	2·821	„	2·482	„
Combined	0·050	„	0·043	„
Total.....	2·871	„	2·525	„
Ash	0·260	„	0·229	„

2nd. Taken October 12th, 1866:—

Weight of 100 berries		138·50 grms.
consisting of skins.....	14·95	
kernels....	8·74	
juice.....	114·81	
		138·50 „

	The juice contained in 100 parts :—		The juice from 100 berries contained therefore :—	
Sugar	12·10	per cent.	13·80	grms.
Acid (calculated as $\bar{T}$ free)	1·493	„	1·722	„
Combined	0·220	„	0·245	„
Total	1·713	„	1·967	„
Ash	0·225	„	0·293	„

3rd. Taken November 16th, 1866 :—

Weight of 100 berries		145·60 grms.
consisting of skins	14·20	
kernels	9·07	
juice	122·33	
		145·60 „

	The juice contained in 100 parts :—		The juice from 100 berries contained therefore :—	
Sugar	16·20	per cent.	19·80	grms.
Acid (calculated as $\bar{T}$ free)	1·333	„	1·651	„
Combined	0·196	„	0·236	„
Total	1.529	„	1·887	„
Ash	0·274	„	0·335	„

Free and combined acids, calculated as tartaric, amount therefore, in 100 parts of juice, to :—

1st	2·871	per cent.
2nd	1·713	„
3rd	1·529	„

In juice from 100 berries :—

1st	2·525	grms.
2nd	1·967	„
3rd	1·887	„

Of these total acids the tartaric acid amounted in reality, in 100 parts of juice, only to :—

1st	0·175	per cent.
2nd	0·141	„
3rd	0·136	„

In juice from 100 berries:—

1st.....	0·154 grms.
2nd	0·162 „
3rd	0·168 „

From the foregoing table it will be seen that although there is a perceptible decrease in the percentage of acid from the first to the second and third samples, there is a decided decrease in the amount of acid present in the juice from 100 berries only, as regards the first sample compared to the second and third, while between the two latter there is only a very slight difference. It will also be noticed that the amount of combined acid is perceptibly greater in the last two samples than in the first. The amount of real tartaric acid precent in the juice from 100 berries shows also a slight increase.

The next three samples of Gutedel were taken from a garden at Darmstadt, September 17th, 1864. They were all taken on the same day and from the same wall, but represented different stages of ripeness. The skins and kernels were not separated; but the berries were analysed as a whole—neither was the combined acid determined.

1st sample—quite unripe.

Weight of 100 berries ..... 106·05 grms.

containing in 100 parts:—

Sugar.....	0·00 per cent.
Free acid, calculated as $\bar{T}$ ..	2·362 „

in 100 berries:—

Sugar.....	0·00 grms.
Free acid, calculated as $\bar{T}$ ..	2·504 „

2nd sample—half ripe.

Weight of 100 berries ..... 136·25 grms.

containing in 100 parts:—

Sugar...	5·76 per cent.
Free acid, calculated as $\bar{T}$ ..	1·582 „

in 100 berries:—

Sugar.....	6·488 grms.
Free acid, calculated as $\bar{T}$ ..	2·155 „

3rd sample—nearly ripe.

Weight of 100 berries .... 279·39 grms.

containing in 100 parts:—

Sugar ..... 8·87 per cent.
Free acid, calculated as $\bar{T}$ .. 0·877 „

in 100 berries:—

Sugar ..... 24·782 grms.
Free acid, calculated as $\bar{T}$ .. 2·450 „

Here, as in the former case, there is a great decrease in the percentage of free acid; but the amount of free acid present in 100 berries is almost the same in the three samples.

Two samples of Muscatel grapes taken from a garden at Dirmstein, from the same wall, and on the same day, October 4th, 1866.

1st (less ripe sample).

Weight of 100 berries ..... 203 grms.

containing in 100 parts:—

Sugar ..... 10·5 per cent.
Free acid, calculated as $\bar{T}$.. 1·255 „

in 100 berries:—

Sugar ..... 21·315 grms.
Free acid, calculated as $\bar{T}$.. 2·547 „

2nd (more ripe sample).

Weight of 100 berries ..... 307 grms.

containing in 100 parts:—

Sugar ..... 15·40 per cent.
Free acid, calculated as $\bar{T}$.. 1·010 „

in 100 berries:—

Sugar ..... 47·278 grms.
Free acid, calculated as $\bar{T}$.. 3·100 „

In this last sample the amount of free acid present in 100 berries has actually increased perceptibly, although the percentage has in all the former samples diminished. If we might assume in the case of the Gutedel and Muscatel, that the amount of combined acid increases with the increasing ripeness,

then the total amount of acid present in 100 berries would show a decided increase with the increasing ripeness instead of a diminution, as has been assumed. Whilst in the case of Riesling we have an augmentation of sugar from 2·63 grm. on September 13th, to 13·80 grm. on October 12th, the total acid, on the other hand, shows a diminution from 2·525 grm. to 1·967 grm. On the other hand, on November 16th, the sugar has risen to 19·8 grms. whilst the acid has sunk only to 1·887 grm., having in fact remained almost stationary.

As regards the samples of Gutedel, the case is even more striking, for here we find an augmentation of sugar from 0·00 grm. in the first sample, to 24·782 grm. in the third, the acid at the same time sinking only from 2·504 grm. to 2·450, or only 0·054 grm., one-fiftieth part.

In presence of the foregoing analyses we are certainly not justified in concluding that in the process of ripening, acid is converted into sugar, although it may possibly be the case. We have then to assume that the conversion of acid into sugar begins at a certain stage of growth, but keeps pace with the production of acid in such a manner as to maintain the total amount of acid present always the same, though the percentage diminishes considerably. It will require however more than a mere assumption to prove such a point. Meanwhile the above analyses point rather to the conclusion that the acid, if it has any thing to do with the production of sugar, does so by virtue of an action similar to that exerted in the conversion of starch into sugar by warm diluted sulphuric acid. The acid is in this latter case suffering no change in the process, a small quantity being capable of producing a large quantity of sugar.

I trust at least to have shown that there is but a slight diminution—and frequently, none—in the total amount of acid present in an entire grape, and that the mere percentage of acid is valueless as an indication of such amount.

In conclusion, my best thanks are due to Professor Büchner, of the Polytechnic School, at Darmstadt, who, by kindly placing his laboratory at my disposal, enabled me to accomplish the greater part of the work given in the preceding notice.

XXXIV.—*Note on Crystallised Glycerin.*

By Dr. J. H. Gladstone.

At the meeting of the Chemical Society, on January 17, Dr. Squire exhibited a large mass of crystals, which had formed part of 5 tons of glycerin that he had received from Germany during the very cold weather of last January. He stated that these crystals slowly melted into good ordinary glycerin containing a small percentage of water; and that when they had once melted, he had never succeeded in re-crystallising the substance, though he had exposed it to long-continued and great cold, had shaken it at the same time, and had immersed unmelted crystals in the cooled liquid.

After the meeting Dr. Squire kindly gave me two or three ounces of these crystals in a corked bottle. They looked very like loaf-sugar which had been moistened with water, and was disintegrated and partially dissolved into syrup. When I reached home, finding the specimen was melting rather rapidly, I put it outside the window. Snow fell that night, and in the morning it appeared to me that there were more crystals inside the bottle than there had been on the previous evening. The specimen was then taken to the laboratory, and being placed on the mantel-piece, in two or three days the crystals had very nearly disappeared, but on removing the bottle to the other end of the room, they began to form again, and in the course of a few days nearly the whole had become a solid mass of transparent crystals. After this they melted again completely; and the liquid then resisted a temperature of about − 18° C. without freezing.

As it was said that this remarkable specimen of glycerin contained sulphoglycerate of sodium, a portion was heated in a platinum crucible. It distilled off, without blackening, until very near the end of the operation, and left an ash weighing only 0·37 per cent. of the original substance. This consisted mainly of alkaline sulphates and chlorides, and from its small quantity can hardly be supposed to have had any influence on the formation of the crystals.

Anniversary Meeting, March 30th, 1867.

Dr. W. A Miller, President, in the chair.

The following Report was read by the President:—

Your Council are glad, on the occasion of another anniversary, to be able to congratulate the Society on its increasing numbers, and on the prosperous condition of its finances.

The number of Fellows on the books at the last annual meeting was 482; at present they amount to 499.

These numbers represent the following state:—

Number of Fellows, March 30, 1866		482
Since elected		49
		531
Removed on account of arrears	14	
Fellows withdrawn	7	
Deceased	11	
	—	32
Number of Fellows, March 30, 1867		499
Number of foreign members, March 30, 1866		37
Since elected		3
Number of foreign members, March 30, 1867		40

The names of the Fellows who have withdrawn are: Robert Barton; J. P. Bidlake; George Lowe, F.R.S.; H. P. Meaden; John Morland; Wm. Payne, junr.; Nathl. Bradley.

The Society has lost by death Dr. Jas. Allan; James Barrett; Thos. De la Rue; E. A. Hadow; W. M. Hindmarch; Fearnside Hudson; P. N. Johnson, F.R.S.; John Mercer, F.R.S.; Simeon Stoikowitsch; Edward Swann; Major Whitmore.

The Council have it under their consideration to raise the standard of qualification for admission to the Fellowship.

During the past year a Committee has been appointed to examine into the state of the Library, with a view of rendering it more complete; and a sum of £100 has been placed at its disposal. The Committee has already added books to the value of £37; besides these, additional works to the value of £28 have been obtained, and these books are in the Library, though not at present paid for.

The Committee are taking steps to complete the sets of such Journals as are at present imperfect. The number of current periodicals which are taken in has also been considerably added to; and a copy of the Memoires d'Arcueil has recently been secured.

James Allan was the younger son of Robert Allan, a surgeon of eminence in Edinburgh, and was born in that city on May 16th, 1825. After receiving a good classical education at the High School, Dumfries, he proceeded in 1842 to the University of Glasgow, where he attended the lectures of Professors T. and J. Thomson. The next six years he spent at Edinburgh, Giessen, and Berlin, studying with Jamieson, Liebig, Mitscherlich, Magnus, Müller, and other great men, who then adorned these schools. He was also for two sessions assistant to Prof. W. Gregory.

Though he made chemistry his chief subject from almost the beginning of his university career, he gained a knowledge of other sciences, which gave a breadth and value to his subsequent teachings. When he was at Giessen he contributed a note to Liebig's Annalen on a "New Zinc Salt;" and in association with Dr. Bensch, published, in the same journal, a memoir on the neutral salts of uric acid.

In 1849, Dr. Allan began to practise as a professional chemist in Manchester, and for some years occupied the Chair of Chemistry in the Pine Street Royal School of Medicine. In 1854 he removed to Sheffield, where he taught in the Wesley College, the Collegiate School, and latterly, in the School of Medicine, and conducted a large analytical practice.

He was very successful as a teacher, and was a clear and fluent lecturer. His pupils were individually attached to him, by the gentlemanly and friendly manner in which he met them. A geniality of disposition and a disinterestedness were com-

bined with his true worth, to form a character, the charm of which will not soon be lost from the memories of his many friends.

He died suddenly on March 19th, 1866, of diphtheric laryngitis, after the tracheometric operation had been performed without avail.

Thomas De La Rue was born in the island of Guernsey in 1793, where he established himself as a printer, publisher, and proprietor of a local newspaper. He subsequently removed to London, and founded the well-known house which now bears his name. Although not a theoretical chemist, he kept himself well informed as to the progress of chemistry, particularly in its applications to the practical arts; and he was himself a persevering and successful investigator of the properties of compounds applicable to the production of dyes and pigments. At the time when he commenced his labours in this direction, Technology was not in its present advanced state, and, as a consequence, those manufacturers who were desirous of surpassing their competitors, had to seek out and produce for themselves, many of the substances required in their processes. The subject of our notice was the first to apply the artificial sulphate of barytes, which he made himself, as a pigment in the preparation of enamelled cards. This was nearly 40 years ago, and since that period many tons have been annually used for that and similar purposes.

At about the same time, he took out a patent for playing cards, and the process thus patented, necessitated the production of printing inks of a highly siccative character, for the inks previously in use would rub off even after the lapse of many years. After infinite trouble he at last succeeded in obtaining the desired result, and thus contributed to the advancement both of typography and of the chemico-mechanical art of lithography. It does not come within the scope of the present article to pass in review his numerous inventions, many of them patented, originated during more than fifty years actively employed in the advancement of the arts; but it may not be out of place to recall two circumstances which will sufficiently show the philosophical bent of his mind. The first is that to him must be assigned the merit of having brought glycerin, till then a waste product, into beneficial use. Even its therapeutic

applications followed from his having called the attention of a medical friend to its healing action on the wounded skin. The second is the fixing of iridescent thin films, which he perfected after thirty years of experimenting.

He was an early, though not an original member of our Society. In the Exhibition of 1851, he was Deputy-Chairman and Reporter of Class XVII., and he was also a Juror of the French Exhibition of 1855, on which occasion he received the distinction of the Legion of Honour.

Mr. De La Rue died at his residence 84, Westbourne Terrace, on June 7th, 1866.

Edward Ash Hadow, youngest son of George John Hadow, Esq., of the Madras Civil Service, was born at Clifton, April 18th, 1831.

His love for science was manifested at a very early age, by his inquisitiveness respecting the composition of things in common use, and was fostered by the perusal of the scientific articles in the Penny and Saturday Magazine, which he studied with unflagging interest.

At about the age of thirteen, he was placed in a private school at Clifton, conducted by the Rev. Mr. Bromby, where his liking for chemistry was rapidly developed. Mr. Bromby, yielding to the propensities of his pupil, gave him free access to his private laboratory. After a time the master discovered that the youthful student spent whole nights in making chemical experiments, and, alas for classics and mathematics! that chemistry had taken firm root in a mind resolute to follow the bent of its own inclinations.

His parents however feared the effect of the earnest study of this science upon a constitution never very robust, and it was some disappointment to them, when the time came that he should decide upon his future profession, to find their son relinquishing Oxford and the Church, and selecting medicine, which appeared to offer the only opportunity for following up his favourite pursuit.

Oxford at that time presented no special attraction to the student of natural science; and it was decided that he should commence his medical curriculum in the usual way in his own city.

He accordingly entered the medical school at Bristol, as a

pupil of Dr. Prichard, then Lecturer on Surgery and Anatomy at the school. In the further prosecution of his studies he received a new impulse from Dr. Wm. Budd, whose scientific zeal and originality of thought attracted the congenial mind of his pupil, and the acquaintance thus commenced ripened into a mutual friendship.

Mr. Hadow matriculated subsequently in the University of London, and he obtained the diploma of the College of Surgeons, but he did not proceed in his University career further than his first examination for the degree of M.B., having been diverted from the profession of medicine by engagements which he subsequently entered into at King's College, London, which school he attended in the further prosecution of his medical studies.

While here he became a successful competitor for the Daniell Scholarship, and the essay which was rewarded on that occasion was his well-known paper on gun-cotton, published in the Journal of this Society for 1854.

In this paper he succeeded in explaining the various contradictory statements up to that time current upon the composition of gun-cotton by showing that a series of substitution compounds exists; and he described the properties of each, and the mode of preparing them—giving proof that these compounds are derivatives of cellulose, in which a certain number of atoms of hydrogen have been displaced by a corresponding number of molecules of nitric peroxide, $N\Theta_2$.

The results of these investigations have since been confirmed by a committee of Chemists in Austria, and most fully by the recent elaborate researches of our Vice-President, Mr. Abel.

Mr. Hadow was an accomplished photographer, and he is well known as joint Editor with Mr. Dawson, of his friend Mr. Hardwich's Manual of Photography.

Shortly after the publication of his paper on gun-cotton, Mr. Hadow was appointed Demonstrator of Chemistry in King's College, a post which he occupied till his death. In 1857 he communicated to this Society a short paper on the detection of alum in bread, in which he indicates a simple method of discovering the adulteration. It consists in immersing a slice of the suspected bread for a few hours in a freshly prepared dilute decoction of logwood, when the red colour of the solution becomes changed in the pores of the bread into a purple dye, which penetrates to some depth. In the following year he gave

a paper on the action of oxidizing agents on the sulphocyanides, and the method of converting them into cyanides. One of the most important of his investigations was that on the composition of the platinicyanides. This paper was communicated to the Society in 1860. He ascertained that the proportion of the cyanogen to the platinum in these compounds was the same in the platinocyanides and in the so-called platinicyanides; and the difference in composition between the two sets of salts, he found to consist in the addition of a certain amount of chlorine, bromine, or other elementary or compound salt-radicle. The salt commonly described as *platinicyanide of potassium* he showed to be really a chloroplatinocyanide ($5K_2PtCy_4,K_2PtCy_4Cl_2.21H_2O$). Two other interesting papers were published by him in the Society's Journal for last year: one on the nitro-prussides, in which he appears to have established for this class of salts the general formula ($M'_4Fe_2Cy_{10}N_2O_3$), and has also given a new method for obtaining the sodium-salt on a large scale without difficulty, the process consisting in mixing a solution of potassic ferricyanide with a regulated quantity of corrosive sublimate, acidulating with acetic acid, and then adding a definite amount of sodic nitrite.

A more laborious work, upon which he had been engaged at intervals for three or four years, was his investigation of the platinum-bases, the proof-sheets of which he revised during his last illness. In this paper he gives directions for the preparation of these compounds in abundance and purity; he confirms the formulæ of Gerhardt for the compounds discovered by Raewsky, and he describes several new compounds, of which the most interesting is a blue salt, obtained by the reaction of nitrous acid upon nitrate of diplatosamine.

Mr. Hadow's manner was singularly unobtrusive, united with great steadiness of purpose and kindness of heart. He was a man of deep religious feelings, ever ready to sympathise with suffering and sorrow, and liberal to the full extent of his means, though few more truly entered into the spirit of the injunction, "when thou doest alms, let not thy left hand know what thy right hand doeth."

While his colleagues lament the loss of a highly valued friend, the members of this Society cannot but feel that his death has deprived them of one whose devotion to chemical science, and whose skill and perseverance promised much for its advancement.

He died of pneumonia, after an illness of several months' duration, on 11th August, 1866, in the 35th year of his age.

William Matthewson Hindmarch, Q.C., the third son of Mr. William Hindmarch, a brewer, in the town of Sunderland, and his wife, Maria Eleanora, daughter of Walter Matthewson, Esq., was born on 10th June, 1803.

He was educated at Sunderland, and as a youth he devoted the chief portion of his hours of recreation to chemistry and mechanics, for the pursuit of which he had fitted up an apartment in his father's house as a laboratory and workshop.

He was afterwards articled to Messrs. Collin and Smart, the eminent solicitors in Sunderland, and having completed his clerkship with them, entered as a student at Gray's Inn, attending at the same time some of the classes in University College.

On the 30th January, 1832, he was called to the bar, and joined the Northern Circuit shortly afterwards. In 1836 he published a supplement to "Deacon's Digest of the Criminal Law of England," and having devoted himself chiefly to the practice of his profession in relation to letters patent for inventions, he, in 1846, published a treatise on the law relating to patent privileges, a work which exhibits much research and learning, and which has been recognised as the best text-book on the subject ever since its publication. In the year 1851, when the question of the amendment of the patent law was agitated, he published a pamphlet containing "Observations on the defects of the Patent Laws, and suggestions for the Reform of them."

This question having again been much discussed in the year 1862, a Royal Commission was issued, on which Mr. Hindmarch, with Lord Stanley, Sir W. P. Wood, Mr. Grove, Mr. Fairbairn, and some others, were appointed.

In November, 1861, Mr. Hindmarch received the appointment of Attorney-General of the County Palatine of Durham, and in the vacation after Hilary Term he was appointed a Queen's Counsel, and shortly afterwards Bencher and Treasurer of Gray's Inn.

In consequence of complaints of disorders in the Patent Office, Mr. Hindmarch and Mr. Greenwood, the solicitor to the Treasury, were appointed, at the instance of the then Lord Chancellor (Lord Westbury), Commissioners to inquire into these complaints, and also to examine into the accounts of that

office. This was a work of great labour, and resulted in three most elaborate reports, which, with the evidence, constitute a blue book of no small dimensions.

At the general election, in March 1865, he unsuccessfully contested the borough of Leominster. In August, in the same year, the Recordership of York was conferred upon him.

Early in 1866, it was apparent to his friends that his health was much impaired; but they hoped that the rest and recreation of his usual vacation tour on the continent would restore him, and in this hope he left London towards the middle of August last.

Having arrived at Aix-la-Chapelle, he exhibited the most alarming symptoms of exhaustion and prostration, and, after four days' illness, he died there on the 27th August, in the 64th year of his age.

Fearnside Hudson, the eldest son of Dr. John Hudson, was born in London in 1837. In childhood he gave unusual evidence of his love for experimental science. At the early age of twelve he gathered around him from the streets large audiences of boys, before whom he lectured and performed chemical experiments. After serving an apprenticeship as analytical chemist with Professor Stone in Manchester, and attending the Medical School in that city, he was placed for two years in the laboratory of the University of Giessen, under Professor Will. On his return to London, he obtained first-class certificates from the Science and Art Department as Science Teacher in Chemistry, Botany, and Vegetable Physiology. He then opened a laboratory, and commenced the first Government Science Classes held in Lancashire.

His skill as an analytical chemist led to his being frequently consulted in cases of poisoning. Mr. Hudson was the author of a work on "Inorganic Chemistry," with the new equivalents and systematic notation. He died at the early age of twenty-nine.

Percival Norton Johnson,* assayer, metallurgist, and refiner, of Hatton Garden, died June 1, 1866, aged 73. He was the eldest son of John Johnson, at one time the only com-

* Particulars kindly furnished by G. Matthey, Esq.

mercial assayer in London; and, after working with his father for some years, he established himself in Hatton Garden, half a century ago.

He rapidly rose to the highest eminence as an assayer and metallurgist, and his opinion was so much sought after, that he could hardly get through the work which crowded upon him.

The extreme accuracy of his assays, viz., in reporting the actual contents of gold and silver, which before had only been done approximatively, soon caused them to be called in question, and to be refused by the buyers of bullion, the advantage in buying upon them not being so great. Upon this being represented to him by the merchants, he at once stated that he was willing, if required, to purchase all bars upon his own assays; and this was the origin of his taking up the refining business, thus, as it were, compulsorily thrown upon him. In this he was so successful, that it has ever since continued to be a very important branch of the Hatton Garden business, and the largest of its kind in the world. His ability in this (as in all other branches that he entered upon) was soon recognised publicly, and when the gold bars from the Brazilian "Gongo Soco" Mines, which came over in very large quantities, were refused at the Mint, on account of *brittleness*, he was consulted on the matter, and undertook to refine and toughen them, in which he succeeded perfectly, and the whole of the Brazilian gold was from that time worked at Hatton Garden.

It was in this gold that he discovered the existence of palladium, and having succeeded in its separation, he introduced it commercially, at once determining and making known the best uses to which it could be applied. At one time he was able to supply this metal at fourteen shillings per ounce. It is now so scarce, that it sometimes realises ten guineas per ounce. He supplied it gratuitously to the Geological Society.

After he had been in business some years, he visited Germany, and was much interested in mining operations there, to which he gave special attention. It was at this time that he met with the compound alloy, called "German Silver," then in a very crude and imperfect state of manufacture. He brought over with him some of the metal, analysed it, and upon the basis of his analysis he commenced its manufacture, with much profit to himself. He was the *first* person in England who made it, and he carried on its manufacture and introduced it to general

use, laying the foundation of the enormous business which has since arisen in this branch of metallurgy. At that time the rough pottery nickel was merely ground and ignited with nitre, the resulting oxide washed and reduced, at the same time that the fusion of the alloying metals was effected. After a few years, owing to his many engagements and the pressure of what he considered his more legitimate work, he undoubtedly neglected the German silver business, which was then most energetically taken up by the Birmingham firm, Evans and Askin, who have ever since retained it almost exclusively in their hands.

About this time he was much engaged and consulted in mining pursuits; and he visited professionally nearly all the mines in England, Wales, Scotland, Ireland, and many important ones abroad. He was the first to introduce in Cornwall the German shaking, jigging, and washing table, with important improvements of his own. He will always be remembered throughout the mining districts for his great kindness and consideration towards the miners, whose social condition it was his constant aim to improve. At great expense to himself he erected schools, &c., in the neighbourhood of the mines, and took an active part in their supervision. He also used his utmost endeavours to alleviate the toil of the miners in ascending and descending mines. With this view he, at the Tamar Mines, made the experiment of a sloping gallery, which ran for a considerable distance under the river, by which means the miners could walk up and down without the use of a ladder.

Amongst his many minor inventions, may be mentioned several pottery colours; amongst them the rose-pink, at a time when that colour was much wanted in the potteries,—the manufacture of which he carried on for many years, at the same time as "Oxide Uranium," a valuable colour much used in glass-making, of which he always maintained the monopoly.

His greatest success, however, and that which has proved the most valuable to the progress of chemistry and manufacture generally, was the platinum business. To him, undoubtedly, belongs the credit of having been the first who successfully refined and manufactured platinum upon a commercial scale, and introduced it for the purposes to which it is specially adapted. The first large and perfect sheet of pure platinum ever produced was made by Mr. Johnson, at 79, Hatton Garden; and

seeing the immense importance of this metal, he ever since made it his specialty.

It is an interesting and, perhaps, not well-known fact, that the real discoverer of the mode of refining and consolidating platinum was, *not* Dr. Wollaston, but Mr. Thomas Cock, a brother-in-law of Mr. Johnson, a gentleman of considerable private means, and a distinguished, though little known amateur chemist and metallurgist. It was in William Allen's laboratories (Plough Court) that he first succeeded in working the metal, and it was at William Allen's special request that he showed his experiments and their results to his friend Dr. Wollaston, then visiting him. Dr. Wollaston adopted this process for the manufacture of platinum, and to him has generally been accorded the credit of having discovered it. Mr. Thomas Cock being much interested in the work at Hatton Garden, spent much of his time in the laboratories there, and Mr. Johnson took up the platinum manufacture, using Mr. Cock's process up to the time of his retiring from business, and always remained the only platinum-refiner in England.

John Mercer, F.R.S., was a remarkable instance of a self-made man. Beginning the world without any advantages derived from education or easy circumstances, he attained, by indomitable energy and perseverance, a considerable position both as a man of science and as a manufacturer. The best portion of his life was devoted to calico printing, to the advancement of which he contributed by the invention of many useful and ingenious processes. He was born February 21st, 1791, at Great Harwood, near Accrington. His father had a small cotton factory, and he himself worked in early youth at the loom. In 1807, being then 16 years old, he was much struck by the bright colour of a child's dress, which was an orange dyed with annotto. The wish to dye this and similar colours possessed him, but he did not know how to begin. In an outline of his life, drawn up by Mr. Mercer for his sons, he says:—"How to begin was my difficulty. There was no fancy dyer in our village; I had no acquaintance with any one who knew anything of dyeing, and I had no books that would help me. The villagers wore mostly dyed cotton at that time, and got them dyed at Blackburn. I therefore went to a druggist at Blackburn, and got a little of all the kinds of stuffs the dyers used, *with*

the names written on each. Weavers at this time having plenty of cotton fents, I was thus well provided with all that was required, and by ringing changes and labelling all the results I was able to dye all the colours then in use. Not having convenience where I lived, I took a man to join me, who had a sufficient building for a dyehouse, with water near, and we dyed for the inhabitants of Great Harwood and the surrounding villages." From 1809–10 Mr. Mercer was employed in the works of Mr. Fort, calico-printer, at Oakenshaw, near Manchester. During the following years he devoted himself with much ardour to the study of chemistry, to which his attention had been directed by the purchase at an old book-stall of a copy of "Parkinson's Pocket Chemistry." He then began to experiment on colours for calico-printing, and at the end of 1817 had succeeded in applying some totally new colours to calico. Amongst these was the orange sulphuret of antimony, a colour so much brighter than the one up to that time dyed with annotto, as immediately to attract the notice of the calico-printers in the neighbourhood. His success led to his appointment as chemist in Mr. Fort's works, at Oakenshaw. In 1825 he was admitted a partner in the concern, and continued in this capacity till 1848, when the firm, having been very successful, gave up the business, Mr. Mercer retiring with a handsome fortune. He thenceforward devoted himself to theoretical chemistry, and was during later years in correspondence with many of the first chemists of the day.

It would be difficult to name all Mr. Mercer's inventions in connection with calico-printing. It may suffice to mention those with which his name is chiefly associated. The long-popular style of manganese-brown, with white discharge and wood-colour illuminations, was his invention, and hundreds of thousands of pieces in this style must have been printed. He contributed largely to the chemistry of indigo-dyeing, and invented an ingenious process for discharging indigo-blue by means of alkali and red prussiate of potash. He was the original maker of dry stannate of soda, now so largely used by calico-printers, Mr. Steiner having previously introduced the liquid stannate of potash, a much more costly article. He was the first to apply arseniates as a substitute for cow's dung in madder-dyeing, phosphates having previously been employed for the same purpose. The chlorinating of woollen fabrics and

mixed fabrics of wool and cotton, whereby a property of seizing and retaining colours with greater facility is given to wool, was, as all printers of these fabrics will admit, a step of very great importance, and had Mr. Mercer patented this invention a very large sum would probably have accrued to him. It was, however, given to the trade with no reservation whatever. To Mr. Mercer must be attributed the discovery of the peculiar action of caustic soda and sulphuric acid upon cotton. This singular process, now called "mercerizing," has the effect of untwisting the normally twisted flattened tubes of cotton filaments and converting them into cylindrical tubes. When colours are applied to the cotton so treated, they pass more readily through the minute pores of the tubes, and are precipitated in denser layers in the interior of the latter, whereby darker and more permanent shades are produced. Calico so treated has become greatly increased in strength, and though hitherto no large quantities of cloth thus prepared have been printed, owing to the expense of preparation, advantage has been taken of the process to prepare the cotton fabric used in the production of the endless web known to calico-printers as the india-rubber blanket, which, when made with prepared calico, is rendered much more durable.

Mr. Mercer acted as a chemical juror for the Great Exhibition of 1851, as well as that of 1862. In 1852 he was elected a Fellow of the Royal Society. He was an honorary member of the Literary and Philosophical Society of Manchester, as well as of the Glasgow Philosophical Society. He was put on the commission of the peace in 1861. Mr. Mercer closed a long period of useful labour on November 30th, 1866, after several years of suffering, borne by him with great fortitude and resignation. He had endeared himself to all who knew him by his simplicity of character, large-hearted kindness, and purity of life. To the poor his hand was always freely extended, and having himself been one of the people, he knew how to sympathise with their sorrows, and give aid where most wanted. Though dying at an advanced age, his loss is felt by a large circle of friends, as that of one whose powers of mind and virtues of heart were of no common order.

Simeon Stoikowitsch was of Hungarian descent, but educated at Paris, to which his parents removed from Peterwardein

during his infancy. He was early admitted into the laboratory of M. Pélouze, where he received an excellent chemical education, and secured the good opinion and kindly interest of his teacher. Mr. Stoikowitsch first came to England as chemical assistant to Professor Calvert of Manchester; and after a year, became assistant to Mr. Graham at the Mint, and continued so for more than five years. He possessed a singular neatness of experimenting, with much readiness of resource in manipulation, and was found a most valuable aid by Mr. Graham. The health of Mr. Stoikowitsch, which was always delicate, gradually gave way, and after returning to his family in Paris, he died in June last, at the early age of 26.

List of Papers read at the Meetings of the Chemical Society, between March 30th, 1866, and March 30th, 1867:—

1. "On the Estimation of Phosphorus in Iron and Steel:" by Mr. J. Spiller.
2. "On Magnesium:" by Prof. Wanklyn and Mr. Chapman.
3. "Note on Mercury-ethyl:" by Mr. E. T. Chapman.
4. "Contribution to the History of the Periodides of the Organic Bases:" by Mr. W. A. Tilden.
5. "On the Formation of Acetylene by Imperfect Combustion:" by Mr. H. McLeod.
6. "On the Synthesis of Guanidine:" by Dr. Hofmann.
7. "On Picric Ether:" by Dr. H. Müller and Dr. Stenhouse.
8. "On Styphnic or Oxipicric Ether:" by Dr. Stenhouse.
9. "On the Water Supply of the Metropolis during the Year 1865—1866:" by Dr. Frankland.
10. Note on Pyrophospho-diamic Acid:" by Dr. Gladstone.
11. "Researches upon the Phosphates of Calcium, and upon the Solubility of Tricalcic Phosphate:" by Robert Warington, Jun., Esq.
12. "Production of Acetic and Propionic Acids from Amylic Alcohol:" by Mr. E. T. Chapman.
13. "On the Oxidation of Ethylamine:" by Prof. Wanklyn and Mr. Chapman.
14. "On the Action of Acids on Naphthylamine:" by Mr. E. T. Chapman.

15. "On some Compounds obtained from Acetone:" by Sir Robert Kane.
16. "On Formulæ for the Expansion of Gases by Heat:" by the Rev. W. B. Gibsone.
17. "On the Nitro-prussides:" by Mr. Hadow.
18. "On the Oxidation-products of the Propione produced from Carbonic Oxide and Sodium:" by Prof. Wanklyn.
19. "On Phthalic Aldehyde:" by Prof. Kolbe and Mr. G. Wirchin.
20. "On Chrysammic Acid:" by Dr. Stenhouse and Dr. H. Müller.
21. "On Chrysammic Ether:" by Dr. Stenhouse.
22. "On the Platinum-bases:" by Mr. Hadow.
23. "On some Decompositions of Nitrite of Amyl:" by Mr. E. T. Chapman.
24. "On a Cyanogen Derivative of Marsh-Gas:" by Mr. Bassett.
25. "On the Action of Acids upon Metals and Alloys:" by Prof. Crace Calvert and Mr. Johnson.
26. "On the Constitution and Representation of Organic Compounds:" by Dr. Williamson.
27. "On the Reduction of the Oxides of Nitrogen in Organic Analysis:" by Mr. W. Thorp.
28. "On some Hydrocarbons contained in Crude Benzol:" by Dr. Schorlemmer.
29. "On Ethyl-hexyl Ether:" by Dr. Schorlemmer.
30. "On an Instrument for taking the Specific Gravities of Heterogeneous Liquids:" by Dr. H. Sprengel.
31. "On the Relation between the Products of Oxidation and the Molecular Constitution of the Bodies Oxidised, Part I.:" by Messrs. E. T. Chapman and W. Thorp.
32. "On Atmospheric Ozone:" by Dr. Daubeny.
33. "On a Chlorosulphide of Carbon:" by Mr. W. N. Hartley.
34. "On the Relation between the Products of Oxidation and the Molecular Constitution of the Bodies Oxidised, Part II.:" by Messrs. E. T. Chapman and W. Thorp.
35. "On the Synthesis of Butylene:" by Mr. E. T. Chapman.
36. "On the Synthesis of Formic Acid:" by Mr. E. T. Chapman.
37. "On the Alloys of Magnesium:" by Mr. Jas. Parkinson.
38. "On the Oxidation of Ethylic Benzoate:" by Mr. R. H. Smith.
39. "On the Basicity of Tartaric Acid:" by Mr. W. H. Perkin.

40. "On the Absorption of Vapours by Charcoal:" by Mr. J. Hunter.
41. "On some Reactions of Hydriodic Acid:" by Mr. E. T. Chapman.
42. "On a New Continuous Aspirator:" by Mr. H. McLeod.
43. "On the Amount of Carbonic Acid contained in Sea Air:" by Mr. E. T. Thorpe.
44. "On the Amount of Carbonic Acid contained in the Atmosphere of Brazil during the rainy season:" by Mr. E. T. Thorpe.
45. "Synthetical Researches on Ethers," Part II. "Action of Sodium and Isopropylic Iodide upon Ethylic Acetate:" by Dr. Frankland and Mr. Duppa.
46. "On the Titration of the Compound Ethers:" by Prof. Wanklyn.
47. "On Quantitative Analysis by Limited Oxidation:" by Messrs E. T. Chapman, and W. H. Smith.
48. "On the Preparation of Berberine from *Coscinium fenestratum*:" by Dr. Stenhouse.
49. "On some varieties of Orchella Weed and Products obtained from them:" by Dr. Stenhouse.
50. "On the Eggs of *Carixa mercenaria*:" by Dr. Phipson.
51. "On Limited Oxidation—Determination of the Oxygen consumed:" by Mr. E. T. Chapman.
52. "On the Oxidation of Formic Acid:" by Mr. E. T. Chapman.
53. "On the Synthesis of Formic and Sulphurous Acids:" by Dr. A. Dupré.
54. "On Phosphonitrile:" by Dr. Gladstone.
55. "On Phosphide of Magnesium:" by Mr. James Parkinson.

The following lectures have also been delivered:—

1. "On the Thermal Phenomena accompanying Chemical Action:" by Prof. G. Carey Foster.
2. "On the Observation of the Course of Chemical Change:" by Mr. A. V. Harcourt.
3. "On the Constitution of some Carbon-compounds:" by Dr. Debus.
4. "On Alloys:" by Dr. Matthiessen.

The following Fellows were elected Officers and Council for the ensuing year:—

President.

Warren De la Rue, Ph.D., F.R.S.

Vice-Presidents who have filled the Office of President.

Sir B. C. Brodie, F.R.S.
C. G. B. Daubeny, M.D., F.R.S.
Thomas Graham, F.R.S.
A. W. Hofmann, LL.D., F.R.S.
W. A. Miller, M.D., F.R.S.
Lyon Playfair, Ph.D., C.B., F.R.S.
A. W. Williamson, Ph.D., F.R.S.
Colonel Philip Yorke, F.R.S.

Vice-Presidents.

F. A. Abel, F.R.S.
Walter Crum, F.R.S.
J. H. Gladstone, Ph.D., F.R.S.
John Stenhouse, LL.D., F.R.S.

Secretaries.

William Odling, M.B., F.R.S.
A. V. Harcourt, M.A.

Foreign Secretary.

E. Frankland, Ph.D., F.R.S.

Treasurer.

Theophilus Redwood, Ph.D.

Other Members of the Council.

J. Lothian Bell.
F. Crace Calvert, F.R.S.
Dugald Campbell.
W. Crookes, F.R.S.
F. Field, F.R.S.
David Forbes, F.R.S.
G. C. Foster.
A. Matthiessen, Ph.D., F.R.S.
H. M. Noad, Ph.D., F.R.S.
W. J. Russell, Ph.D.
Maxwell Simpson, Ph.D., F.R.S.
J. A. Wanklyn.

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY.

Drs. **Crs.**

1866-7.		£	s.	d.	1866-7.		£	s.	d.	£	s.	d.
March 29.	To Balance on hand, 25th March, 1866			762	8	11	Journal.	By Editor's Salary		95	0	0			
	,, Dividends on £1,800 Consols			45	14	6		,, Printing Journal		193	13	6			
	,, Sale of Journals (2 years)			95	2	1		,, Distributing ditto		52	16	11			
	,, Sale of Museum Specimens			13	10	7		,, Reporting Proceedings		17	17	0			
	,, Sundry Receipts from 27th March, 1866, to 29th March, 1867:—												359	7	5
		£	s.	d				,, Proceedings of Royal Society					50	0	0
	Admission Fees	98	0	0			Library.	,, Librarian's Salary		25	0	0			
	Life Compositions	130	0	0				,, Books and Magazines		37	5	6			
	12 Subscriptions for 1865 and previous years	25	0	0				,, Bookbinding		13	8	9			
	97 Subscriptions for 1866	166	0	0									75	14	3
	300 Subscriptions for 1867	513	0	0			Collector and Clerk	,, Collector's Commission		46	12	0			
				932	0	0		,, Gratuity to Mr. West for making list of Fellows		3	3	0			
								,, Clerk		3	0	0			
													52	15	0
								,, Stationery, Stamps, &c.					19	18	7
							House Expenses.	,, Tea at Meetings:—							
								To Royal Society		16	7	8			
								To Mr. Hux		0	18	2			
								,, T. J. Hux, Salary		20	0	0			
								,, ,, Petty Expenses		2	2	11			
								,, Gas		2	13	0			
								,, Coals		2	10	0			
								,, W. Page, Cleaning		1	1	0			
								,, Gate Porter		2	2	0			
								,, ,, Coat		3	0	0			
													50	14	9
								,, Purchase of £500 3 per Cent. Consols					438	2	6
								,, Balance at Messrs. Coutts' Bank					802	3	7
			£	1848	16	1			£				1848	16	1

Assets.

	£	s.	d.
Balance at Coutts'	802	3	7
Invested in Three per Cent. Consols	1800	0	0
	£2,602	3	7

We have examined the accounts of the Chemical Society from the 25th of March, 1866. to the 29th of March, 1867, inclusive, compared them with the vouchers, and found them correct. We find the balance in favour of the Society to be £802 16*s.* 1*d.*, which is at the bankers. From the statement of the Treasurer it appears that the outstanding subscriptions due to the Society amount to £250.

March 29th, 1867.

B. F. DUPPA,
EDMUND J. MILLS, } *Auditors.*

XXXV.—*On some of the effects produced by the addition of Plaster of Paris to Must.*

By A. Dupré, Ph.D.

If report speaks truly, it is the almost universal practice in Spain, Portugal, and the South of France, to add plaster of Paris to the grape-juice in the process of wine-making. The plaster is generally thrown upon the grapes before they are crushed, or it is added after fermentation has already begun.

The reason generally advanced in favour of this addition is, that the plaster, by uniting with some water of the grape-juice, renders the remaining juice richer in sugar, and thus more valuable. A chemist will scarcely require to be told that if such be really the intention, the desired effect will not be obtained to any degree worth considering, since even perfectly pure plaster of Paris unites with only a little more than a quarter of its weight of water, while on the other hand, the gypsum thus formed takes up mechanically a considerable quantity of liquid, thereby reducing the yield to the like amount.

In order, however, to render the subject clear in this respect to the general public, I have been induced to undertake the following experiments:—

The juice experimented on was pressed from grapes imported into the London market as Lisbon grapes, 48 ounces of which yielded 32 ounces of juice.

Two ounces of juice being reserved for examination, the rest was divided into three quantities of 10 ounces, to which were added 1, 2, and 5 ounces of plaster of Paris respectively, or 10, 20, and 50 per cent. The plaster of Paris was added in small quantities, well stirred into the juice, and then allowed to remain in contact with it for 24 hours. At the end of that time the clear juice was poured off the precipitate, the latter placed upon a cloth and pressed to get out as much juice as possible. The juice to which 50 per cent. of plaster had been added had quite solidified, and no juice could be obtained without pressing. In this manner 9 oz., 8 oz., and 4·3 oz. of juice were recovered of the 10 ounces taken in each case. The original juice and the three samples treated, were then examined for sugar, free acid, and, in two cases, for the amount of tartaric acid and ash. The

results are given in the following table; the figures given show the amount of substance present in 1 litre of the juice.

Original juice contained in 1 litre :—

137·58 grms. sugar.
5·07 grms. free acid calculated as $\overline{T}$.

Juice with 10 per cent. plaster. Amount of juice recovered, 90 per cent., containing in 1 litre :—

138·38 grms. sugar.
4·57 grms. free acid calculated as $\overline{T}$.

Juice with 20 per cent. plaster. Amount of juice recovered, 80 per cent., containing in 1 litre :—

143·96 grms. sugar.
3·35 grms. free acid calculated as $\overline{T}$.

Juice with 50 per cent. plaster. Amount of juice recovered, 43 per cent., containing in 1 litre:—

154·54 grms. sugar.
0·66 grm. free acid calculated as $\overline{T}$.

It will be seen from the above that the addition of plaster increases the percentage of the sugar, but diminishes the amount of juice. Taking the two effects into consideration, we arrive at the following calculation :—

Amount of sugar in 1 litre of juice.....					137·58	grms.
Amount of sugar in juice recovered from 1 litre after the addition of	10	per cent.	plaster	....	125·44	„
Do.	do.	20	per cent.	„	115·16	„
Do.	do.	50	per cent.	„	66·45	„

In the last case, therefore, more than half the sugar contained in the original juice had to be sacrificed in order to raise the percentage of the remaining part from 13·75 to 15·45; truly a miserably small gain for so large an expenditure. The same increase in sugar might have been obtained by the addition of 2 per cent. of sugar, or by the evaporation of 11·1 per cent. of water. In the first case, 2 per cent. more juice would have resulted: in the second case, a loss of only 11·1 per cent. as against 57 per cent. loss by the use of plaster of Paris for the like increase in the amount of sugar.

Roughly speaking, we may conclude from the above that plaster of Paris, added to grape-juice, combines chemically with a quarter of its weight of water, the gypsum so formed absorbing its own weight of juice, which cannot be recovered by pressing. In other words, for each grm. of sugar gained, four grms. are lost on account of diminished yield. Nor is this loss made good, even if the gypsum is allowed to ferment with the must, the only difference being, that whereas in the first case the gypsum retains must, in the latter case wine remains absorbed, the relative loss being as great as before. But this greatly diminished yield is not the only drawback connected with the plastering of wine. The gypsum, as is well known, decomposes the tartrate of potassium present in the juice, insoluble tartrate of calcium being formed, and sulphate of potassium going into the solution. At the same time, the carbonate of calcium, always present, in greater or smaller quantity, in plaster of Paris, precipitates the free tartaric acid, besides neutralising some of the other free acids of the juice, and, if present in sufficient quantity, even neutralising them completely, when the phosphates of the juice will also be precipitated.

The addition of plaster of Paris, therefore, tends to the more or less complete removal of the tartaric acid, one of the most characteristic constituents of grape-juice, leaving only free or combined malic acid, an acid which grape-juice has in common with all other sour fruits. The place of the cream of tartar is taken by sulphate of potassium, a salt having a perceptibly bitter taste, and acting as a purgative, even in moderately large doses.

Moreover, as it seems probable that the amount of tartaric acid present in grape-juice increases with the increasing ripeness of the grape, whilst the malic acid diminishes in amount, the plastering virtually reduces the juice of even the ripest grapes to a state of unripeness, as regards the nature of the acids at least.

In the above samples, the amount of tartaric acid present in the original juice amounted to 0·916 grm. per litre, which in the case of the juice with 20 per cent. plaster added, had been reduced to 0·01 grm., the amount of malic acid remaining the same in each.

The original juice yielded 4·085 grms. ash per litre, containing 2·415 grms. carbonate of potassium; the juice to which the

20 per cent. plaster had been added, yielded 7·255 grms. ash, containing 0·005 grm. carbonate of potassium per litre.

Some experiments undertaken in which the plaster was allowed to ferment with the crushed grapes, completely confirm the foregoing conclusions.

Three quantities of 20 ounces each were taken. They were crushed in a mortar, and placed in flasks, which could be closed by a mercury-valve so as to allow the escape of carbonic acid, but prevent the free entry of atmospheric air. The first lot (No. I.) was allowed to ferment by itself; to the second (No. II.) one ounce of plaster was added before fermentation began; to the third lot (No. III.) 2 ounces of plaster were added, or 5 per cent. and 10 per cent. respectively. After fermentation had ceased, they were analysed, and any sugar yet unfermented was calculated as yielding its equivalent of alcohol, which was added to the alcohol found. Besides this, the amounts of tartaric acid, ash, and carbonate of potassium in the ash, were estimated.

The juice before fermentation contained 14·0 per cent. sugar, and 0·236 per cent. tartaric acid. It left 0·390 per cent. ash, containing 0·207 per cent. carbonate of potassium.

No. I. yielded, on pressing, 78·75 per cent. of the weight of the grapes taken as wine, which contained 6·12 per cent. alcohol and 0·208 per cent. tartaric acid, and left 0·343 per cent. ash, with 0·138 per cent. carbonate of potassium.

No. II. yielded, on pressing, 76·25 per cent. of the weight of the grapes taken as wine, which contained 6·17 per cent. alcohol and 0·090 per cent. tartaric acid, and left 0·603 per cent. ash, with 0·013 per cent. carbonate of potassium.

No. III. yielded, on pressing, 71·25 per cent. of the weight of the grapes taken as wine, which contained 6·36 per cent. alcohol and 0·071 per cent. tartaric acid, and left 0·620 per cent. ash, with 0·013 per cent. carbonate of potassium.

Taking the yield of No. I. (the grapes without any addition) as 100, with 6·12 parts of alcohol, the yield of No. II. will be 96·82, with 5·97 alcohol, and of No. III. 90·4, with 5·75 alcohol. Loss of alcohol in No. II., 2·5 per cent. of total yield of No. I.; loss in No. III., 6 per cent. of total yield in No. I.

The increase in ash in No. II. and No. III. is due chiefly to the conversion of carbonate of potassium into sulphate of potassium; in part, also, to the solubility of the plaster of Paris.

In presence of the very general custom of the countries above named of adding plaster of Paris to the grapes or the must, it would be unsafe to conclude from the foregoing that the addition of plaster is of necessity only hurtful, my chief object being to show that the very generally received opinion as to its object cannot be a sound one, since nobody could be supposed knowingly to waste so much for so small a gain; and, secondly, to draw the attention of some chemist residing in any of the aforenamed countries once more to this subject, as it seems to me some considerable advantage will have to be shown to accrue from this practice, to justify so serious a loss and deterioration of the juice as is shown in the preceding to follow the plastering. We may, however, safely conclude from the foregoing, and take as a guide in the analysis of wine, that all wines during the production of which plaster of Paris has been used, will be characterized, firstly, by a more or less complete absence of tartaric acid; secondly, by a large proportion of ash, which latter will be very poor in carbonate, but very rich in sulphates. Perfectly pure plaster of Paris removes only that part of the tartaric acid united to potassa; the complete removal is effected by the carbonate of calcium.

XXXVI.—*On the practical loss of Soda in the Alkali Manufacture.*

By C. R. A. Wright, B.Sc., Private Assistant in the Chemical Laboratory at St. Thomas's Hospital.

The experiments, the results of which follow, were recently conducted by the author on the large scale in a works capable of producing upwards of 150 tons of soda-ash weekly, and extended over a period of several months. Manufacturing operations not admitting of the precision with which laboratory experiments may be conducted, the results can only be expected to be approximate. During this period the capabilities of production of the plant were strained to the utmost, so that in many instances the losses indicated are probably the largest at all consistent with remunerative work.

Fair samples of each day's make of salt-cake, black-ash, soda-ash, &c., &c., were taken by the writer, and carefully sealed up.

At the end of two or three weeks, as occasion served, these daily samples were respectively mixed together and carefully analysed. It may not be out of place to remark here that when the alkalimetric value (or percentage of available alkali) of a sample was determined, the error occasioned by the neutralization of normal acid by any alumina or lime present was uniformly eliminated by first adding a slight excess of standard acid, and heating to incipient ebullition with litmus tincture. On adding a slight excess of standard sodic carbonate solution, a lake was precipitated, and the excess of sodic carbonate added was determined in the filtered liquid. When this precaution was not adopted, the amount of available alkali indicated was found to be uniformly higher than that really present. In determining the sodic salts in vat-waste, a gravimetric determination is indispensable, as the waste always becomes more or less oxidized during or before the laboratory operations, and the calcic sulphate thus produced re-acts on the sodic carbonate present, yielding sodic sulphate, which would thus be neglected in a volumetric determination.

A few experiments on the loss of sodic compounds in the transformation of salt into salt-cake showed that this is practically inappreciable. The amount of loss (average) deduced from the weights and analyses of salt and salt-cake, was 0·47 per cent.; that is, for every 100 parts of sodium employed as salt, 99·53 parts were practically obtained as salt-cake. From analysis of the condensed hydrochloric acid, it appeared that 0·18 per cent. of the sodium employed was mechanically carried over to the condensers by the current of gas (blind furnaces).

The salt-cake was converted into black-ash by using limestone and slack in the usual proportions, viz.:

Salt-cake, 100 parts.
Limestone, 100—110 parts.
Slack, 62—65 parts.

The black-ash was lixiviated as rapidly as possible, rarely remaining above two days in stock. The vat liquor, after settling, was oxidized to destroy sulphide, and boiled down to a pasty mass. This, being thrown on to a strainer, furnished "salts" (which, on drying, became "refined ash") and "red liquor," which, on admixture with fresh vat-liquor and boiling down to dryness, yielded "soda-ash."

It was found that 100 parts of salt-cake of the annexed average composition yielded on an average 151·7 parts of black-ash of the composition given in the column A (and yielding about 58 per cent. of dry waste on lixiviation); and also yielded 46·523 parts of soda-ash, together with 16·015 of refined ash, the average composition of these being as given below.

The column B of the black-ash gives the analysis of one fortnight's average make of black-ash, and column B of the vat-waste gives the composition of the waste made from this black-ash. Reference will again be made to these two analyses.

Average Composition of Salt-cake, Black-ash, and Soda-ash.

	Salt-cake.	Black-ash.		Soda-ash.	Refined ash.	Dried vat-waste.	
		A.	B.			A.	B.
Na_2SO_4	87·33	2·06	1·42	3·59	4·39		
$NaHSO_4$	3·77						
Na_2CO_3	..	39·64*	40·19	62·60	87·44	{2·22† / 5·57‡}	5·08
NaHO	..	..	..	11·28	1·02		
Na_2SiO_3	..	..	1·46	0·76	0·65		
$Na_2Al_2O_4$	..	..	0·92	0·43	0·64		
Na_2S	..	..	..	traces	nil		
Na_2SO_3	..	..	..	1·68	0·53		
$Na_2S_2O_3$	..	..	..	0·34	traces		
NaCl	5·31	3·02	3·01	8·14	3·56	..	nil
Na_4FeCy_6	..	..	..	0·18	nil		
CaO	..	..	5·63	..	..	..	1·85
CaS	..	..	30·26	..	..	..	35·91
$CaSO_4$	1·91	..	..	..	..	..	1·32
$CaCO_3$	..	..	6·03	traces	traces	..	27·10
$MgSO_4$	traces						
Fe_2O_3	0·61	..	..	0·16	0·38		
Insoluble Al_2O_3: & P_2O_5: & Fe_2O_3	..	..	3·00	..	..	..	5·33
Sand	0·50	..	..	0·05	0·17		
Sand and Coke	..	..	7·78	..	..	..	23·14
Moisture	0·37	..	..	10·97	0·93		
Undetermined and loss	0·20	..	0·30	..	0·29	..	0·27
	100·00	..	100·00	100·18	100·00	..	100·00
Total available Na_2SO_4	89·56						
„ „ Na_2O	..	23·18	24·57	48·32	54·37		

* This represents the total available alkali soluble in water, calculated as Na_2CO_3.

† This represents the total soluble sodic salts, calculated as Na_2CO_3.

‡ This represents the total sodic salts soluble and insoluble, calculated as Na_2CO_3.

(A.) 100 parts of salt-cake containing 89·56 of available Na_2SO_4, should theoretically yield 39·104 of Na_2O, supposing all the Na_2SO_4 converted into compounds capable of neutralizing test-acid; practically however, only 31·189 parts of available alkali were obtained in the state of marketable soda-ash; hence the total loss in converting salt-cake into soda-ash has been 7·915 parts out of 39·104, or 20·24 per cent.

(B.) 100 parts of salt-cake yielding 151·7 of black-ash, containing 23·18 per cent. of available alkali, there was obtained 35·164 parts of alkali soluble in water in the form of black-ash; hence the loss in the various stages previous to lixiviation amounts to 3·940 parts out of 39·104, or to 10·07 per cent.

As a proof of the approximate exactness of these two numbers it may be mentioned that similar determinations, with slightly different charges in the black-ash furnaces, and during different periods, yielded the following results:

Total loss in converting salt-cake into soda-ash.	Loss previous to lixiviation.
20·7	10·8
20·0	9·75

These losses are chiefly made up by the following circumstances :—

(α.) Non-conversion of Na_2SO_4 into Na_2CO_3.

(β.) Formation of sodic compounds insoluble in water and consequently left in the waste, in addition to the Na_2CO_3 left there by deficient washing.

(γ.) Volatilization of sodic compounds in the black-ash furnace and sinkage into the brickwork of the furnace.

(δ.) Deficient extraction of soluble sodic compounds during lixiviation.

(ϵ.) Formation of sodic sulphide during lixiviation, and subsequent oxidation to sulphate.

(ζ.) Formation of insoluble sodic compounds subsequent to lixiviation, leakage during evaporation, &c., sinkage of sodic salts into the brickwork of the white-ash furnaces, and the mechanical effect of a current of hot air passing over a boiling liquid, or a wet substance drying, in removing small vesicles and particles spurted up.

(α.) 100 parts of salt-cake containing 89·56 of available Na_2SO_4 yielded 151·7 of black-ash, containing 2·06 per cent. of Na_2SO_4;

hence containing 3·125 parts of Na_2SO_4 out of the original 89·56; hence the loss of sodic sulphate unconverted into carbonate was 3·49 per cent.

(β.) The average amount of sodic salts expressed as Na_2CO_3 contained in vat-waste in a state soluble in water was 2·22 per cent.; whilst the total amount (soluble and insoluble) was 5·57 per cent.; consequently sodic salts representing 3·35 per cent. of Na_2CO_3 in the waste must have existed in a state insoluble in water. 100 parts of black-ash (representing 39·64 of soluble Na_2CO_3) yield 58 of waste, containing therefore 1·94 of insoluble Na_2CO_3 (or its equivalent). Hence the proportion between the insoluble sodic compounds in the waste to the soluble ones in the black-ash, is that between 1·94 and 39·64, or 4·90 per cent.; as the soluble salts in the black-ash however only represent 100 − 10·07, or 89·93 per cent. of the original salt-cake, the total loss from the formation of insoluble sodic compounds was 5·44 per cent. This point will be again referred to.

(γ.) It was found impossible to get any definite idea as to the magnitude of the loss experienced by volatilization of sodic compounds in the black-ash furnace, or by sinkage into the brick-work; these two sources together must however practically be inconsiderable (with well worked furnaces in good order) inasmuch as 5·44 + 3·49 or 8·93 parts of loss out of the original 10·07 previous to lixiviation have been already accounted for.

It may be noticed that an appreciable volatilization of NaCl appeared to take place in the black-ash furnace: 100 parts of salt-cake contain 5·31 of NaCl; and yield 151·7 of black-ash containing 3·02 per cent. of NaCl, representing therefore 4·56 parts of NaCl; as it cannot well be supposed that any chloride was converted into carbonate in the furnace, it appears that about one-seventh of the original NaCl was volatilized.*

(δ.) 100 parts of black-ash (containing 39·64 per cent. of soluble Na_2CO_3) yielded 58 of waste containing 2·22 per cent. of soluble sodic salts expressed as Na_2CO_3, and hence representing 1·29 parts of Na_2CO_3.

Hence 1·29 parts of the 39·64 in the black-ash, or 3·25 per

* While this paper was in course of preparation, a letter from Mr. James Hargreaves appeared in the Chemical News (Nos. 387 and 388), calling attention to this and other points noticed here: possibly the white cloud visible on opening the door of a black-ash furnace, and referred to by him, may be mainly due to vapour of sodic chloride.

cent. was lost by deficient lixiviation; as the soluble alkali in the black-ash represents only 89·93 per cent. of the original salt-cake, the total loss from deficient lixiviation was 3·61 per cent.

(ε.) The loss by formation of sulphate during and after lixiviation was practically inappreciable; in fact was less than the experimental errors, thus:

	Ratio of Na_2SO_4 to available Alkali.	
Black-ash	2·06 to 23·18	or 8·9 to 100.
Soda-ash	3·59 to 48·32	or 7·5 to 100.
Refined-ash ..	4·39 to 54·37	or 8·1 to 100.

Apparently the oxidation was only just sufficient to produce sulphite and hyposulphite; in fact, it might be questioned whether in a hot strongly alkaline liquid any sulphate would be formed until the whole of the hyposulphite was converted into sulphite, as the sulphite may be supposed to be the primary oxidation product of sulphide, and the hyposulphite to be produced by a secondary action between the sulphite and the still unoxidized sulphide.

Analyses of the vat-liquor showed that the ratio of the sodium combined as sulphide to that in the form of available alkali was on an average 2·20 to 100.

(ζ.) The loss by formation of sulphate being inappreciable, and that by deficient lixiviation being 3·61, the loss during evaporation, &c., will amount to 6·56 per cent.

It was found impossible to get any very exact knowledge of the precise amount of loss due to any of the smaller causes going to make up this total; it was however noticed that during the evaporation of oxidized vat-liquor in an open pan, a crystalline deposit was formed at the bottom of the pan, which on drying was found to have the following composition:

Sand and coke-dust	3·5
Combined SiO_2	15·0
„ Al_2O_3	14·0
Na_2O, not as carbonate	5·5
Na_2CO_3	49·8
NaCl	6·2
Na_2SO_4	3·7
Fe_2O_3	1·0
$CaCO_3$	1·3
	100·0

It is hence manifest that a considerable portion of sodium was combined as alumino-silicate; this was quite insoluble in water.*

Several experiments, conducted with a view to ascertain the amount of loss of soda in the drying furnace, showed that with a newly-built furnace the total loss amounted to 4·35 per cent. of the amount passed through; after being some months in use, the loss in the same furnace amounted to only 0·12 per cent.

Hence, probably, this latter represents the mechanical effect of the current of hot air in mechanically removing particles, while the majority of the former amount is due to the absorption of substance by the brickwork of the furnace.

New furnaces for the evaporation of liquors, paved with iron bricks, were found to yield about one-tenth less ash than that yielded by a precisely similar old furnace from the same amount of the same liquor; showing again a considerable absorption by the materials of the furnace.

It hence appears that the amounts of loss due to these several causes may be approximately tabulated thus:—

Previous to lixiviation	Undecomposed sodic sulphate.....	3·49
	Insoluble sodic compounds	5·44
	Vaporisation, &c., of sodic compounds	1·14
During and after lixiviation	Soluble alkali left in vat-waste	3·61
	Oxidation of sulphide	—
	Leakage and losses in white-ash process	6·56
		20·24

On the whole therefore it appears that the two largest sources of loss were the formation in the black-ash of insoluble sodic compounds, and the leakage and other losses in the white-ash process.

In order to gain some insight into the composition of this insoluble sodic compound, a sample of the black-ash manufactured during one entire fortnight was carefully analysed (B. p. 409), and treated as follows:—

A known weight was treated with 50 parts of water at varying temperatures and for varying times. After filtration from

* The formation of insoluble sodic aluminic silicates is remarked by Mr. Hargreaves in the paper previously referred to (Chem. News, 387). Kynaston also noticed the precipitation of aluminic sodic silicate on boiling an aqueous lixiviate of black-ash (Chem. Soc. J. 11, 135).

the insoluble residue, and washing, the total sodium dissolved out was carefully determined, and after subtraction of the amounts due to NaCl and Na_2SO_4, calculated as Na_2O, with the following results:—

	Length of time in contact.	Temperature.	% of Na_2O.
(A)	3 hours	20° C.	23·56
(B)	48 „	do.	23·77
(C)	3 „	60°—70° C.	23·87
(D)	6 „	do.	23·82
(E)	30 minutes	Boiling constantly: water replaced as it evaporated	23·66
(F)	6 hours	do.	24·64

The insoluble residue of (F), dissolved in hydrochloric acid and the sodium estimated gravimetrically, yielded only traces of Na_2O.

That of (C), treated in the same way, yielded 0·84 per cent. of Na_2O, thus indicating a total of 24·71 per cent. of Na_2O.

The total percentage of Na_2O existing otherwise than as chloride or sulphate was found by the analysis of the black-ash (B. p. 409) to be 24·57.

From these numbers it is evident that there was in the black-ash a sodic compound not attacked by cold or warm water, even on long digestion, nor even by boiling water when the action was only of short duration; but decomposible on continued ebullition, yielding a sodic salt capable of neutralizing acid.

It is clear that this compound could not be chloride, as it existed in the waste, where no chloride is present, and from its alkaline reaction. Experiment showed that exactly the same percentage of sulphate was obtained whether the black-ash were simply lixiviated with cold water, or entirely dissolved in hydrochloric acid (care being of course taken to prevent the formation of any sulphate by oxidation). It is possible that it might exist as an alumino-silicate, though it hardly appears probable that such a compound would be formed in presence of so large an amount of extra alkali as exists in black-ash; but from the well known fact that on causticizing sodic carbonate by quick-lime, the calcic carbonate formed retains a considerable portion of sodium in a state not extractable by water, it appears more probable that a double sodic calcic carbonate is formed, either in the furnace or on the addition of water to the black-ash.

Some experimental black-ash charges having been worked containing much more limestone than usual (135 of limestone to 100 of salt-cake), the resulting black-ash was examined to see if more of this insoluble compound were formed: there was found 20·75 per cent. of available alkali extractable by water, and in the perfectly washed residue 0·85 per cent. of Na_2O, incapable of solution in cold or warm water.

Somewhat similar experiments were performed with the average sample of vat-waste obtained from the former fortnight's work of black-ash: a known weight was treated just as the black-ash, and the dissolved alkaline salts estimated gravimetrically, and a complete analysis was made (B. p. 409).

Length of time in contact.	Temperature.	Total Na dissolved out calculated as Na_2CO_3.
15 hours	20° C.	3·56
5 minutes	Boiling constantly	3·58
6 hours	Do. water replaced as it evaporated.	3·81

From the complete analysis it appears that sodic salts equivalent to 5·08 per cent. of Na_2CO_3 were present. It appears therefore that although six hours' boiling has effected a slight decomposition of the insoluble compound, yet the majority remained unattacked; possibly the difference between the black-ash and the waste in this respect may be due to the influence of the other sodic salts in the former on the insoluble compound.

XXXVII.—*Description of an Apparatus for preventing Escape of Sulphuretted Hydrogen.*

By The Rev. B. W. GIBSONE, M.A., B.Sc.

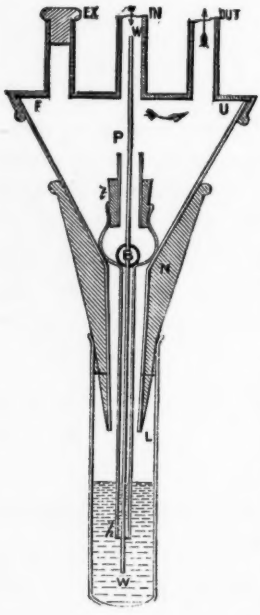
THIS apparatus consists of the three following parts:—

I. *The Generator.*—This part of the apparatus has been described by me in the Chemical News, and is a simple arrangement for controlling the generation of gas or stopping it speedily when not required; it consists merely of the ordinary generator and wash-bottle, connected by an extra syphon-tube,

which latter acts so as to convert the wash-bottle into a reservoir for the exciting acid, when gas is not required.

II. *The Absorber.*—Is only an arrangement of three successive Woulfe's bottles charged with *liquor ammoniæ* or *liquor potassæ*, to absorb all gas unused after the required saturation of any fluid with hydric sulphide; the ammonic or potassic sulphide thus generated may be employed again as a source of the gas, or as a useful reagent in other processes.*

III. *The Adapter.*—The principal subject of this paper is a sort of universal bung capable of being fitted closely into the mouth of any common vessel containing liquid to be treated with hydric sulphide, of supplying it with the gas, and of affording suitable exit to the surplus; it commences delivery only after attachment, and ceases on being detached.



FUNL is a funnel, containing within it a second funnel (say a thistle-head) *t h*, whose leg will easily traverse the leg NL of the larger, allowing windage between; the smaller funnel in turn contains the bullet B, of gutta-percha pierced diametrically by the thin glass rod or platinum wire WW, which latter will similarly slide up and down freely within *th*, allowing airway, and will serve as a guide-rod and trigger.

The thistle-head is terminated upwards by a short open glass pipe P, attached by a pierced cork or capsule.

The mouth of the large funnel FU, is closed by a caoutchouc cap having three necks; the central of these IN, is the inlet conducting the gas from the generator, and is vertically above P, so that P can slide into it closely when occasion requires forming an air-tight connexion. Of the two outer outlets EX and OUT, one only is used at a time (say OUT), and leads to the absorber, the other being closed by a plug till it is alternately wanted to connect a freshly-charged absorber.

Finally, round the large funnel are coiled strips of india-

* It may advantageously be converted into ammonic acetate.

rubber, till it forms from end to end a gradually increasing, continuous, elastic cone, which will hermetically close the cylindrical mouth of any moderately-sized receptacle (such as a test-tube) containing the liquor to be analysed.

The apparatus may be continually traversed by the gas, when not in use for analysis, as shown in the figure. The bullet B, by its weight, then acts as a valve, closing the throat of the thistle-head-funnel, which itself in turn closes the throat of the larger funnel; no delivery consequently takes place at L or *h*, but the current passes directly, as shown by the arrows, in at IN and out at OUT or EX, as the case may be.

When the adapter is used for charging any liquid, the test-tube used and its contents are slid upwards vertically over the lower ends *h* and L, till the latter is securely corked by the caoutchouc coating of the larger funnel; by this action the bottom of the test-tube raises first the guide-rod W, and attached bullet; and, secondly, thrusts the smaller funnel up till its summit P securely closes the elastic inlet IN; the two valves are thus opened, *h* beneath the liquid and L above it; the gas is then wholly diverted down the inside of the smaller funnel, through the liquid, and up between the two funnels, passing out as before at OUT.

When the operation is complete, the test-tube is withdrawn, the valves fall into their former position, and the direct current is re-established.

Various minor items, such as suitable packings for the valves, or removable delivery-pipes, will be contrived by each constructor, according to the size and capabilities of his materials.

As with the best of contrivances, there may be some leakage at the valves, I prefer always to keep an empty test-tube affixed *in situ*, as in the figure, when not using the instrument.

There is nothing ordinarily to prevent two, three, or even half-a-dozen such adapters being connected successively, each in turn fed by the same current of gas, and each saturating its own solution, provided only that the absorber close the series.

If such an arrangement were in common use, our better laboratories might furnish the bench of every student with a supply of hydric sulphide, laid on by pipes from some central source, similarly to coal-gas and water.

XXXVIII.—*On some new Derivatives of the Hydride of Salicyl.*

By W. H. PERKIN, F.R.S.

A SHORT time since I published a paper in the "Laboratory," on some salicyl derivatives,* in which I stated that the hydride of salicyl appeared to possess the properties of an alcohol (or hydrate of a hydrocarbon-radical) as well as those of an aldehyde. In confirmation of this view, it was shown that if the equivalent of hydrogen, which is assumed to be alcoholic, be replaced by benzoyl, the resulting body still possesses the properties of an aldehyde, whereas had the typical hydrogen of the aldehyde been replaced, the resulting body would no longer have retained this character, but would have been a mixed acid radical, benzoyl-salicyl.

On extending my experiments in this direction, I have succeeded in obtaining several new substances—derivatives of the hydride of salicyl containing alcohol-radicals, an account of which I beg to lay before the Society.

HYDRIDE OF METHYL-SALICYL.

When coarsely powdered hydride of sodium-salicyl (salicylite of sodium) is heated to 135°—140° C. in a sealed tube, with rather more than its own weight of iodide of methyl, and from two to three times its bulk of alcohol, it gradually disappears, the contents of the tube becoming perfectly clear, and of a pale brownish colour. This change generally takes place in the course of two or three hours. On opening the tube and diluting its contents with water, an oil separates; this is to be well washed with dilute hydrate of potassium, to remove any hydride of salicyl that may be present. It is then collected, transferred to a retort, and distilled. At first a small quantity of iodide of methyl and water comes over, after which the thermometer rapidly rises to 238° C., and the remainder distils as a nearly colourless oil, within two or three degrees of that temperature.

* Laboratory, vol. i, p. 51.

This product is pure *hydride of methyl-salicyl*. Two combustions of this substance gave the following numbers :—

I. ·2168 of substance gave
·5601 of CO_2, and
·1193 of H_2O.

II. ·1876 of substance gave
·4855 of CO_2, and
·1040 of H_2O.

These numbers give percentages which agree well with those required by the formula—

$$H,C_7H_4(CH_3)O_2 = C_8H_8O_2.$$

The following is a comparison of the theoretical and experimental numbers :—

	Theory.		Experiment.	
			I.	II.
C_8	96	70·59	70·45	70·58
H_8	8	5·88	6·11	6·15
O_2	32	23·53	—	—
	136	100·00		

The formation of this substance may be expressed thus :—

$$\left(\begin{matrix}CO'',H\\C_6H''_4\\Na\end{matrix}\right\}O\right) + MeI = \left(\begin{matrix}CO'',H\\C_6H''_4\\Me\end{matrix}\right\}O\right) + NaI$$

Hydride of sodium-salicyl (salicylite of sodium). Hydride of methyl-salicyl.

The hydride of methyl-salicyl is a nearly colourless oil, boiling at 238° C., and possessing only a very slight odour. It is heavier than water, and insoluble or nearly so in that liquid. When cooled in a mixture of ice and salt, it does not solidify. If brought in contact with sodium, it evolves hydrogen and apparently forms a new compound.

The hydride of methyl-salicyl is isomeric with the hydride of anisyl, but differs from it both in boiling point and odour. It is an aldehyde, and combines with the bisulphites.

Bisulphite of Potassium and Hydride of Methyl-salicyl.

On agitating these two bodies together, the mixture becomes warm, and a beautiful crystalline compound rapidly forms. This product crystallises in splendid prisms from a mixture of alcohol and water.

It is very soluble in cold water; difficultly soluble in cold, but more so in hot alcohol. It is decomposed when heated, and also when treated with a solution of hydrate of potassium. It has a very burning taste.

Bisulphite of Sodium and Hydride of Methyl-salicyl.

A strong solution of bisulphite of sodium dissolves this hydride with evolution of heat, and on standing deposits crystals of the new compound, which is very soluble in water. On evaporating its solution in vacuo, it is left as a confused crystalline mass.

Bisulphite of Ammonium and Hydride of Methyl-salicyl.

On mixing this hydride with a strong solution of bisulphite of ammonium, heat is evolved, and a clear syrupy liquid is produced, which in the course of ten or twelve hours, becomes filled with splendid transparent prisms of the new compound, half an inch in length. They are very brilliant, and resemble small crystals of sulphate of sodium. This compound is easily soluble in cold alcohol and in water.

Action of Bromine on the Hydride of Methyl-salicyl.

When bromine is added drop by drop to the hydride of methyl-salicyl, heat is evolved, and large quantities of hydrobromic acid are given off. After an excess of this reagent has been added, and all action has ceased, the product, on being well agitated with a solution of hydrate of potassium, until free from excess of bromine, presents itself as a nearly white solid. This, when washed with water and dissolved in boiling alcohol, crystallises out on cooling in beautiful flat oblique prisms, which may be further purified by a second crystallisation. A combustion of this substance gave the following numbers:—

·1926 of substance gave
·3150 of CO_2 and
·0621 of H_2O.

These results give percentages agreeing well with those required by the formula

$$H,C_7H_3Br(CH_3)O_2 = C_8H_7BrO_2,$$

as the following comparison will show:—

		Theory.		Experiment.
C_8	=	96	44·65	44·60
H_7	=	7	3·25	3·58
Br	=	80	37·20	—
O_2	=	32	14·90	—
		215	100·00	

This body is therefore the hydride of methyl-salicyl with one equivalent of hydrogen replaced by bromine. I therefore propose to call it the *hydride of methyl-bromosalicyl.*

The hydride of methyl-bromosalicyl crystallises from boiling alcohol in splendid flat prisms. It melts at 113°—114,5° C. It is difficultly soluble in cold alcohol, but very soluble in hot alcohol.

Action of Ammonia on the Hydride of Methyl-salicyl.

A mixture of the hydride of methyl-salicyl and alcoholic ammonia, when left to stand for 24 hours, becomes syrupy, and on being evaporated, spontaneously yields a viscid product. This would appear to be a substance corresponding to hydrobenzamide. I have not succeeded in obtaining it in a crystalline condition.* When heated for a few hours to 160°—170° it is

* In one experiment I obtained a quantity of a beautiful transparent crystalline body containing

C..... 69·91 p. c.
H..... 7·51

I have not, however, succeeded in reproducing this substance. It is very soluble in alcohol when heated in the water-oven fuses, and on cooling forms a transparent resin.

converted into an organic base, forming with perchloride of platinum a yellow salt.

Action of Nitric Acid on the Hydride of Methyl-salicyl.

When mixed with nitric acid 1·4 sp. gr. this hydride dissolves, forming a yellow liquid, which rapidly changes colour, and after standing for a few minutes, evolves a small quantity of red fumes. The action then sets in rather energetically, the mixture at the same time becoming very warm. When cool, the addition of water causes a dark-coloured oil to separate, which is heavier than water. This body appears to be the *hydride of methyl-nitrosalicyl.*

If digested with a fresh quantity of nitric acid, this nitro-compound decomposes and yields a solid nitro-acid. When pure, this product has a pale-yellow colour. It is soluble in boiling water, from which it crystallises on cooling; it also dissolves readily in solutions of the carbonates of sodium and potassium, forming salts. In all probability this substance is *methyl-nitrosalicylic acid.*

HYDRIDE OF ETHYL-SALICYL.

This body is produced in precisely the same manner as the methyl derivative, only substituting iodide of ethyl for that of methyl, and collecting the portion which distils between 246°·5 and 249° C. Two combustions of this product gave the following numbers:—

I. ·1978 of substance gave
·5210 of CO_2 and
·1202 of H_2O.

II. ·2431 of substance gave
·6405 of CO_2 and
·1483 of H_2O.

These give percentages agreeing closely with those required by the formula—

$$H,C_7H_4(C_2H_5)O_2 = C_9H_{10}O_2,$$

as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C_9	108	72·00	71·83	71·85
H_{10}	10	6·66	6·75	6·77
O_2	32	21·34	—	—
	150	100·00		

The formation of this substance is analogous to that of the hydride of methyl-salicyl.

The hydride of ethyl-salicyl is a nearly colourless oil, boiling at 247°—249° C. It refracts light strongly, and possesses but little odour at the ordinary temperature. It is heavier than water, and, if cooled with a mixture of ice and salt, does not solidify. With alcohol or ether it mixes in all proportions, but is insoluble, or nearly so, in water. Unlike the hydride of salicyl, it does not combine with alkalies, though it still possesses the properties of an aldehyde.

Bisulphite of Sodium and Hydride of Ethyl-salicyl.

On mixing a saturated solution of bisulphite of sodium with about its own volume of the hydride of ethyl-salicyl, no change at first appears to take place, but after agitating for several minutes, the mixture becomes an almost solid mass of crystals. To purify this product, it is to be well drained from the excess of bisulphite, and pressed between bibulous paper, first with the hand and then with a screw-press. After being dried in vacuo, it is dissolved in warm alcohol, filtered, and the solution evaporated spontaneously or in vacuo; by this means it is obtained as silky needles. If crystallised from water over sulphuric acid, it is deposited in splendid prisms, three-quarters of an inch in length. These, at first, are nearly transparent, but gradually become opaque, and effloresce when exposed to the air, owing to the loss of water of crystallisation. A portion dried in vacuo over sulphuric acid until constant in weight, when ignited with sulphuric acid, gave the following results:—

·2590 of substance gave
·0690 of sulphate of sodium = 8·63 per cent. of sodium.

The formula $C_9H_{10}O_2,HNaSO_3$, requires 9·05 per cent. of sodium.

Heated to 100° C., this compound decomposes, and on the addition of water, oily globules of the hydride separate. It is also decomposed by hydrochloric acid and hydrate of potassium. When dissolved in water, it produces a slightly turbid solution, possessing a very burning taste.

Bisulphite of Ammonium and Hydride of Ethyl-salicyl.

A strong solution of bisulphite of ammonium, when shaken up with this aldehyde, quickly combines with it, the resulting compound separating as a beautiful crystalline mass. The excess of bisulphite of ammonium may be removed from this product by pressure between bibulous paper.

This compound is rather less soluble in water than the preceding bisulphite of sodium derivative; it is also rather difficultly soluble in alcohol. When dissolved in water it appears to undergo slight decomposition, and, if heated in the water-oven, it softens and swells up. Hydrochloric acid and also alkalies decompose it. It crystallises in transparent, flat prisms, having rectangular terminations. These crystals appear very beautiful when viewed by means of a microscope fitted with Nichol's prisms.

Action of Bromine on the Hydride of Ethyl-salicyl.

With bromine this hydride behaves in precisely the same manner as the hydride of methyl-salicyl, producing a beautiful crystalline derivative. Two combustions of this product gave the following results:—

I.	·1442 of substance gave ·2478 of CO_2, and ·0578 of H_2O.
II.	·1922 of substance gave ·3319 of CO_2, and ·0739 of H_2O.

These numbers give percentages agreeing with those required by the formula

$$H,C_7H_3Br(C_2H_5)O_2 = C_9H_9BrO_2,$$

as the following comparisons will show :—

	Theory.		Experiment.	
			I.	II.
C_9	108	47·16	46·86	47·09
H_9	9	3·93	4·45	4·27
Br	80	34·93	—	—
O_2	32	13·98	—	—
	229	100·00		

I propose to call this substance the *hydride of ethyl-bromosalicyl.* It crystallises from boiling alcohol (in which it is very soluble) as slightly opaque, flat, oblique prisms. It is but little soluble in cold alcohol. When heated it melts to a colourless oil, and this, on cooling, solidifies, forming a splendid radiated crystalline mass. Its melting-point is from 67° to 68° C. With bisulphite of sodium it forms a crystalline compound, easily decomposed with hydrochloric acid or alkalies.

Action of Ammonia on the Hydride of Ethyl-salicyl.

A solution of this hydride in alcoholic ammonia becomes turbid after standing for three or four hours, and gradually deposits a viscid oil. This, however, gradually changes, and in the course of ten or twelve hours becomes converted into a crystalline solid. Stirring accelerates the change. After being thoroughly broken up and washed with cold alcohol, this new body is obtained pure. When burnt in oxygen, it gave the following numbers :—

·2084 of substance gave
·5749 of CO_2, and
·1367 of H_2O.

These numbers give percentages agreeing well with those required by the formula—

$$C_{27}H_{30}N_2O_3,$$

as the following comparisons will show :—

	Theory.		Experiment.
C_{27}	324	75·34	75·23
H_{30}	30	6·97	7·28
N_2	28	6·51	—
O_2	48	11·18	—
	430	100·00	

This substance I propose to call *Hydroethylsalicylamide*. Its formation may be thus expressed :—

$$\underset{\text{Hydride of ethyl-salicyl.}}{3C_9H_{10}O_2} + 2H_3N = \underset{\text{Hydroethylsalicylamide.}}{C_{27}H_{30}N_2O_3} + 3H_2O.$$

It evidently corresponds to hydrosalicylamide, in which three equivalents of hydrogen are replaced by ethyl.

Hydroethylsalicylamide is difficultly soluble in cold, but easily soluble in hot alcohol, from which it crystallises, on cooling, in small but brilliant, oblique prisms ; a portion of product, however, appears to undergo decomposition every time it is recrystallised. Heated in the water-oven, it fuses to a colourless oil, which, when cool, becomes a resinous mass. It dissolves in hydrochloric acid, but is quite insoluble in a cold solution of hydrate of potassium or sodium.

Action of Heat upon Hydroethylsalicylamide.

This substance, when submitted to a high temperature, is completely changed, being converted into an organic base, just as hydroanisamide is converted into anisine or hydrobenzamide into amarine.

A quantity of hydroethylsalicylamide was placed in an open tube and heated in the oil-bath to 160°—165° C. ; this temperature being maintained for about two hours. The substance at first melted to a colourless oil, but gradually assumed a pale-brown colour ; it remained, however, perfectly transparent. On cooling it solidified to a resinous mass, which was dissolved in alcohol acidified with hydrochloric acid, and evaporated to dryness. The amorphous mass thus obtained was perfectly soluble

in boiling water, from which a large quantity deposited, upon the solution cooling, as a gummy mass. On redissolving this product in water and adding a solution of hydrate of potassium, a new base was thrown down as a curdy precipitate. On stirring with a glass rod, this changed into a sticky mass, capable of being drawn into threads. On cooling, however, it became hard, but remained perfectly amorphous.

I propose to call this base *Ethylsalidine*. Its formula appears to be exactly the same as hydroethylsalicylamide, viz. :—

$$C_{27}H_{30}N_2O_3.$$

The hydrochlorate of ethylsalidine is a perfectly amorphous substance, easily soluble in boiling water and very soluble in alcohol. Its solutions possess a very bitter taste.

Platinum-salt of Ethylsalidine.—On adding a solution of perchloride of platinum to an aqueous solution of the hydrochlorate of ethyl-salidine, a precipitate is immediately produced, which, on being stirred, becomes a sticky mass; but if an alcoholic solution be employed, no precipitate is at first formed; but on stirring a small quantity of a platinum-salt separates as a crystalline powder—the quantity increasing as the alcohol evaporates. The method I have found best for the preparation of this salt, is to mix an alcoholic solution of the hydrochlorate containing an excess of acid, with a solution of perchloride of platinum, previously mixed with about twice its volume of alcohol, then to pour the mixture into a shallow glass vessel, and allow it to evaporate spontaneously, when all or nearly all the alcohol has evaporated; the precipitate which has formed is mixed with water, thrown on a filter, well washed, and then dried, first in vacuo and afterwards at 100° C. In this manner it is obtained as a pale orange-coloured, slightly crystalline powder.

A platinum-determination in a specimen prepared as above, gave the following result:—

·3012 of substance gave
·0475 of platinum = 15·77 p. c.

The formula $C_{27}H_{30}N_2O_3,HPtCl_3$, requires 15·513 per cent.

Ethylsalidine also forms a compound with chloride of gold.

Action of Nitric Acid upon the Hydride of Ethyl-salicyl.

On mixing this hydride with nitric acid of 1·4 sp. gr., it changes in colour, and, after a short time, evolves red fumes, the action rapidly becoming more energetic. The addition of water to this mixture causes the separation of a dark-yellow oil, heavier than water. This is apparently the hydride of ethyl-nitrosalicyl.

This nitro-compound, when digested with concentrated nitric acid, evolves a large quantity of red fumes, and, on throwing the mixture into water, a crystalline body is deposited, consisting of a new nitro-acid. To purify this, it is dissolved in a solution of carbonate of soda and filtered from any insoluble residue; dilute nitric acid is then added, which causes the new product to separate. This is collected upon a filter, washed, dried, and, finally, crystallised from alcohol.

A combustion of this product gave the following numbers:—

·1147 of substance gave
·2163 of CO_2, and
·0477 of H_2O.

These numbers yield percentages agreeing with the formula—

$$C_9H_9NO_5.$$

The following is a comparison of the theoretical and experimental numbers:—

		Theory.	Experiment.
C_9	108	51·18	51·43
H_9	9	4·26	4·62
N	14	6·63	—
O_5	80	37·93	—
	211	100·00	

The above formula represents ethylnitrosalicylic acid.

$$C_9H_9NO_5 = C_7H_4(NO_2)(C_2H_5)O_3.$$

Its formation may easily be understood, if we assume that

the first product of the action of nitric acid upon the hydride of ethyl-salicyl is a nitro-compound; thus—

$$\underset{\text{Hydride of ethyl-salicyl.}}{C_7H_4(C_2H_5)O_2} + HNO_3 = \underset{\text{Hydride of nitro-ethylsalicyl.}}{C_7H_4(NO_2)(C_2H_5)O_2} + H_2O.$$

$$C_7H_4(NO_2)(C_2H_5)O_2 + O = \underset{\text{Ethylnitrosalicylic acid.}}{C_7H_4(NO_2)(C_2H_5)O_3}$$

The second stage of this reaction is here simply regarded as that of oxidation, and is analogous to the formation of acetic acid from aldehyde.

This acid corresponds to Gräbe's ethyl-salicylic acid, with one equivalent of hydrogen replaced by NO_2.

Ethylnitro-salicylic acid crystallises from alcohol in large, flattened prisms of a pale-yellow colour, and from water in small, but brilliant prisms. It fuses at 163° C. It is a powerful acid, and reddens litmus strongly. In taste it is both acid and bitter.

Its silver salt is a pale-yellow precipitate.

Iodide of allyl and hydride of sodium-salicyl, when heated together with alcohol in a sealed tube, yield iodide of sodium and an oily product, apparently the hydride of allyl-salicyl.

Iodide of amyl and hydride of sodium-salicyl also, when heated with alcohol in a sealed tube to 150°—160° for a few hours, yield a new aldehyde, which may be purified by combining it with bisulphite of sodium and decomposing the resulting body with hydrate of potassium. It is a very pale-yellow oil, possessing an amylic odour, and, doubtless, is the hydride of amyl-salicyl. Its compound with bisulphite of sodium is very beautiful, crystallising in flat prisms; rather difficultly soluble in water.

From the foregoing results it is seen that the replacement by alcohol-radicals of the hydrogen which I have been induced to regard as alcoholic in the hydride of salicyl, has not in any manner interfered with its aldehydic characters.

It might be argued that ketones sometimes possess many of the characters of aldehyde, and that, therefore, these new bodies might be of that class. This, however, is shown not to be the case, by the formation of ethylnitrosalicylic acid.

On treating the aldehydes of the aromatic series with am-

monia, a remarkable class of bodies is produced, of which hydrobenzamide may be taken as a type. These substances do not retain any of the aldehydic properties of hydrides from which they have been derived. They represent two equivalents of ammonia, in which all the hydrogen is replaced by three diatomic* radicals consisting of the residues of the aldehydes from which they have been formed. This will be better seen from the following equation, showing the formation of hydrobenzamide.

$$3\begin{pmatrix}CO,H\\C_6H_5\end{pmatrix} + 2H_3N = \left.\begin{matrix}\begin{pmatrix}C,H\\C_6H_5\end{pmatrix}''\\\begin{pmatrix}C,H\\C_6H_5\end{pmatrix}''\\\begin{pmatrix}C,H\\C_6H_5\end{pmatrix}'\end{matrix}\right\}N_2 + 3H_2O.$$

These products do not combine with alkalies, being insoluble in their cold aqueous solutions; neither do they form metallic substitution-products, there being no replaceable hydrogen in their constitution. There is, however, one remarkable exception to this rule, and that is in the case of *hydrosalicylamide*—the product derived from hydride of salicyl. This body dissolves freely in solutions of the alkalies, and also produces copper, iron, and other metallic derivatives, their composition showing hydrosalicylamide to contain *three* equivalents of hydrogen replaceable by metals. The copper and cuprammonic derivative has the following composition :—

* This appears to be the case from the interesting experiments of Hugo Schiff, who finds that oil of bitter almonds yields with toluylene-diamine, a substance isomeric with hydrobenzamide; this he designates *toluylene-dibenzylene-diamine*, and assigns to it the following constitution :—

$$\left.\begin{matrix}\alpha\ C_7H^6\\\beta\ C_7H_6\\\beta\ C_7H_6\end{matrix}\right\}N_2.$$

This $\beta\ C_7H_6$ evidently represents the same residue of the hydride of benzoyl as that contained in hydrobenzamide, and this new substance when heated to 140°—159° C. for some time becomes modified, and converted into the same body as hydrobenzamide does, when treated in a similar manner, viz., *amarine*, thus showing, I think, that the residue of the hydride of benzoyl contained in these two substances, is isomeric with diatomic toluylene, and when heated its constituents become more closely united, and thus changed into the more stable radical toluylene. Hugo Schiff evidently regards it as *benzylene*. This appears to me scarcely probable, on account of the ease with which hydrobenzamide yields the hydride of benzoyle when treated with acids benzylene we should expect to be too stable a body to admit of this change.

$$C_{21}H_{15}Cu_2{}^*(NH_3Cu)N_2O_3.$$

It is interesting to find that this peculiarity in the properties of hydrosalicylamide is absolutely required, if the hydride of salicyl possesses the double properties I have assigned to it —even to the number of replaceable equivalents of hydrogen. The following equation will show this:—

$$3\left(\begin{matrix}CO,H\\C_6H_4\\H\end{matrix}\right\}O\Big) + 2H_3N = \left.\begin{matrix}\left(\begin{matrix}C,H\\C_6H_4\\H\end{matrix}\right\}O\Big)''\\\left(\begin{matrix}C,H\\C_6H_4\\H\end{matrix}\right\}O\Big)''\\\left(\begin{matrix}C,H\\C_6H_4\\H\end{matrix}\right\}O\Big)''\end{matrix}\right\}N_2 + 3H_2O.$$

Hydride of salicyl. Hydro-salicylamide.

The metallic derivatives would be represented thus—

$$\left.\begin{matrix}\left(\begin{matrix}C,H\\C_6H_4\\M\end{matrix}\right\}O\Big)''\\\left(\begin{matrix}C,H\\C_6H_4\\M\end{matrix}\right\}O\Big)''\\\left(\begin{matrix}C,H\\C_6H_4\\M\end{matrix}\right\}O\Big)''\end{matrix}\right\}N_2.$$

This characteristic difference in the properties of hydrosalicylamide, appears to me to show almost more clearly than any other facts we are acquainted with, the twofold character of the aldehyde from which it is derived, seeing that in its formation the aldehydic nature of the hydride of salicyl has been destroyed, yet its properties, as an alcohol or hydrate, still remain.

It may be worth remarking, that hydroethyl-salicylamide, described in this paper, does not dissolve in alkalies, nor yet form metallic substitution-derivatives. These facts are quite in harmony with the foregoing reasoning. Its formation may be thus expressed:—

* The old equivalent of copper, viz., 32, has been retained for simplicity's sake.

$$3\left(\begin{matrix}\mathrm{CO,H}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big) + 2\mathrm{H_3N} = \left.\begin{matrix}\left(\begin{matrix}\mathrm{C,H}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big)''\\ \left(\begin{matrix}\mathrm{C,H}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big)''\\ \left(\begin{matrix}\mathrm{C,H}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big)''\end{matrix}\right\}\mathrm{N_2} + 3\mathrm{H_2O}.$$

Thus showing the alcoholic hydrogen to be replaced by ethyl.

The hydrides of methyl and ethyl-salicyl are the aldehydes corresponding to methyl and ethyl-salicylic acids.

$\left(\begin{matrix}\mathrm{CO,H}\\ \mathrm{C_6H_4}\\ \mathrm{Me}\end{matrix}\right\}\mathrm{O}\Big)$ Hydride of methyl-salicyl.

$\left(\begin{matrix}\mathrm{CO,HO}\\ \mathrm{C_6H_4}\\ \mathrm{Me}\end{matrix}\right\}\mathrm{O}\Big)$ Methyl-salicylic acid.

$\left(\begin{matrix}\mathrm{CO,H}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big)$ Hydride of ethyl-salicyl.

$\left(\begin{matrix}\mathrm{CO,HO}\\ \mathrm{C_6H_4}\\ \mathrm{E}\end{matrix}\right\}\mathrm{O}\Big)$ Ethyl-salicylic acid.

The following is a list of the new bodies analysed and described in this paper:—

Hydride of methyl-salicyl	$C_8H_8O_2$.
„ methylbromo-salicyl	$C_8H_7BrO_2$.
„ ethyl-salicyl	$C_9H_{10}O_2$.
„ ethyl-salicyl and bisulphite of sodium	$C_9H_{10}O_2,HNaSO_3$.
Hydride of ethylbromo-salicyl	$C_9H_9BrO_2$.
Hydroethylsalicylamide	$C_{27}H_{30}N_2O_3$.
Hydrochloroplatinate of ethyl-salidine	$C_{27}H_{30}N_2O_3,HPtCl_3$.
Ethylnitro-salicylic acid	$C_9H_9(NO_2)O_3$.

XXXIX.—*Action of Chloride of Iodine on Picric Acid.*

By JOHN STENHOUSE, LL.D., F.R.S.

I HAVE already stated,* that when picric acid is digested with a strong aqueous solution of chloride of iodine, chloropicrin and chloranil are formed. From the manner, however, in which the experiment was then conducted, any other chlorinated products formed at the same time, could not be conveniently isolated. In the experiment just quoted, from the absence of any iodine-compound, it seemed that the chlorine was the active agent in the reaction between chloride of iodine and picric acid—the iodine merely serving as a sort of carrier for the chlorine.

Dinitrochlorophenic Acid.

From some experiments I have recently made, I found the following to be the most convenient method of treating picric acid with chloride of iodine:—3 parts of picric acid, 3 parts of water, and 1 part of iodine were introduced into a flask furnished with two tubes, one serving as a condensing-tube, and the other reaching nearly to the bottom of the vessel, through which a current of chlorine was passed. The contents of the flask were kept gently boiling, whilst chlorine was passed through it for some hours. In a short time, oily drops of chloropicrin condensed in the tube, but these gradually disappeared, and carbonic anhydride and nitric oxide were given off, together with a small quantity of nitrous fumes. The current of chlorine was then stopped, and the chloride of iodine distilled off as far as possible, in a paraffin-bath at about 120°—130° C. If, however, the reaction with chloride of iodine be continued sufficiently long, chloranil is the sole fixed product.

The crystalline residue, after being washed with a small quantity of cold water, is boiled with a considerable quantity of pure water, filtered, and allowed to crystallise. As the acid is but difficultly soluble, even in boiling water, the undissolved portion remaining on the filter should be extracted with the mother-liquors, from which the acid has separated by crystallisa-

* Chem. Soc. Jour. xvii, 332.

tion. The nearly pure crystals of the acid thus obtained, are readily purified by one or two recrystallisations from boiling water.

The acid melts at 103°, volatilises slightly at 100° C., and more readily in the vapours of boiling water. It separates almost entirely from its aqueous solutions when they are strongly acidulated with nitric or hydrochloric acids.

The acid, dried at 100° C., was subjected to analysis, with the following results:—

I. ·468 grm. acid, gave ·561 grm. carbonic acid, and ·067 grm. water.

II. ·185 grm. acid, gave ·121 grm. chloride of silver.

			Theory.	I.	II.
C_6	=	72	32·95	32·91	—
H_3	=	3	1·37	1·59	—
Cl	=	35·5	16·25		16·18
N_2	=	28	12·81		
O_5	=	80	36·62		
		218·5	100·00		

This agrees with the formula $C_6H_2Cl(NO_2)_2.H.O.$

Dinitrochlorophenate of Silver.

This salt was prepared by neutralising a boiling solution of dinitrochlorophenic acid with argentic carbonate. The silver-salt, after recrystallisation, was dried at 100° C., and analysed.

I. ·260 grm. silver-salt, precipitated by hydrochloric acid, gave ·114 grm. argentic chloride.

II. ·494 grm. gave ·216 grm. argentic chloride.

			Theory.	I.	II.
$C_6H_2Cl(NO_2)_2O$	=	217·5	66·83	—	—
Ag	=	108·0	33·17	33·00	32·92
		325·5	100·00		

It will be seen, from these results, that the acid obtained by the above-described process is identical in composition with the dinitrochlorophenic acid of Griess*, with which it also agrees in all its properties.

* Ann. Chem. Phar., cix, 286.

Having submitted a specimen of the acid to Dr. Griess, he informed me that on comparing it with specimens of the dinitrochlorophenic acid, prepared by himself, "he found them the same in every respect." On treating the dinitrochlorophenic acid with sulphide of ammonium, it was converted into *amidonitrochlorophenic acid*, which is also identical with that obtained by Griess.

Dr. Griess's process for preparing dinitrochlorophenic acid consists, as is well known, in chlorinating phenol, and treating the resulting product with nitric acid. The red, oily mass thus obtained, is purified by converting it into the ammonium-salt. This method is tedious, and by no means productive, and, therefore, very inferior to the process with picric acid, above described.

Action of Chloride of Iodine on Styphnic Acid.

When styphnic acid is treated with chloride of iodine in a similar manner to picric acid, it undergoes a very different kind of decomposition, being apparently resolved into chloropicrin and carbonic acid, no chlorinated acid or chloranil being produced. This result confirms the observation I have already made,* "that styphnic acid is not, as Erdmann erroneously supposed, merely oxidated picric acid, but must have a different nucleus, entirely unconnected with that of picric acid."

XL.—*On Pyrophosphoric Acid.*

By Dr. J. H. Gladstone, Ph.D., F.R.S.

In the classic research of Graham, pyrophosphoric acid was viewed as a bibasic acid, having the constitution $2HO.PO_5$; but under the present view, that the atomic weight of oxygen is 16, we are compelled to recognize in it the existence of two atoms of phosphorus, and to assign to it the formula $2H_2O.P_2O_5$, or rather $P_2H_4O_7$. This makes it a quadribasic acid, and that

* Chem. Soc. Jour., xix, 238.

it actually is such, is indicated by its giving some double salts, in which the two metals exist in the proportion of 3 atoms of the one to 1 atom of the other. A still better proof of the above formula may be found in the fact that amides of pyrophosphoric acid exist, in which 1, 2, and 3 molecules of HO are replaced by NH_2.

It is my intention to treat in this paper of—1st. Some normal pyrophosphates; 2ndly. An allotropic modification of these salts; and, 3rdly, the formation of pyrophosphoric acid, and the theory of its constitution.

Normal Salts.

If solutions of a silver-salt and of pyrophosphate of sodium be mixed in any proportion, a permanent white precipitate is the result; but if a solution of ferric chloride be added in small quantity to a solution of pyrophosphate of sodium, the white precipitate, produced at the moment of contact, dissolves in the excess of sodium-salt. If more ferric chloride be added, a permanent, flocculent precipitate is obtained. If the addition be continued, the solid pyrophosphate is again dissolved, but now by the excess of ferric salt.

On performing this experiment with solutions of known strength, it was found that the pyrophosphate of sodium continued to dissolve the iron-salt, till the proportion of two atoms of ferric chloride, feCl,* to one of pyrophosphate of sodium, $P_2Na_4O_7$, was arrived at; then the permanent precipitate increased, with a milky appearance, until the proportion became four to one, at which time no more iron was found in solution, and the ferric salt separated readily in flocculent masses. To dissolve this up again, many atoms of ferric chloride were found to be necessary.

This suggests the existence of a soluble double salt, $P_2Na_2fe_2O_7$; and an insoluble normal pyrophosphate, $P_2fe_4O_7$.

Schwarzenberg†, long ago, gave the above, plus 3 atoms of water, as the composition of ferric pyrophosphate, and the following analyses confirm the conclusion:—

I. 0·330 grm., dried at 100° C., and heated to low redness,

* To avoid great complexity of formulæ, I have adopted Williamson's ferricum with the atomic weight 18·66, and the symbol fe.

† Ann. Ch. Pharm., lxv, 153.

gave off water, losing 0·058 grm. The residue boiled long with hydrochloric acid, and precipitated by magnesium-salt in the presence of citric acid, gave 0·234 grm. of pyrophosphate of magnesium.

II. 0·349 grm. gave 0·245 of pyrophosphate of magnesium.

	Calculated.	Found.	
		I.	II.
Phosphorus	20·48	19·78	19·60
Iron.....	24·65	—	—
Oxygen	37·03	—	—
Water.....	17·84	17·57	—
	100·00		

The supposed double salt, $P_2Na_2fe_2O_7$, being in solution, and mixed with chloride of sodium, and, possibly, other combinations, could not be satisfactorily examined. An attempt was made to separate it by dialysis. It was soon evident that the double salt remained in the dialyser, while the chloride of sodium passed through; but when the chlorine had practically disappeared, the salt partially gelatinized. The whole contents of the dialyser were, nevertheless, evaporated down, and the phosphorus, iron, and water were estimated. There was also a considerable amount of sodium, which could be determined by difference; but the numbers obtained did not agree well with the above formula.

In the reactions described above, I have spoken of ferric chloride and pyrophosphate of sodium, but the iron may be combined with other acids, or potassium may be substituted for the other alkali, without affecting the results.

If a cupric salt be mixed with a soluble pyrophosphate, the precipitate first produced dissolves in excess of the phosphorus-compound, giving a deep-blue solution. On the further addition of copper, a permanent green salt separates, which was found, on analysis, to be the normal pyrophosphate, $P_2Cu_4O_7$, combined with two atoms of water.

I. 0·359 grm., dried at 100° C., and heated to low redness, gave off water, and lost 0·041 grm. The residue was boiled long with hydrochloric acid, and gave 0·238 pyrophosphate of magnesium. The copper had previously been separated by hydrosulphuric acid, and yielded 0·170 grm. of oxide.

II. 0·344 grm. lost 0·038 grm. when heated.

III. 0·378 grm. of a different preparation, lost 0·041 grm. when heated, and gave 0·250 grm. of pyrophosphate of magnesium, and 0·177 grm. of oxide of copper.

These numbers indicate the composition $P_2Cu_4O_7.2H_2O$.

	Calculated.	Found.		
		I.	II.	III.
Phosphorus	18·43	18·51	—	18·47
Copper....	37·57	37·78	—	37·36
Oxygen ..	33·29	—	—	—
Water	10·71	11·42	11·04	10·84
	100·00			

An attempt was made to isolate the double pyrophosphate of copper and sodium by dialysis, but it passed through the parchment paper about as readily as the sulphate of sodium did.

Excess of pyrophosphate of sodium is also capable of dissolving the precipitates produced by it with mercurous, ferrous, zinc, aluminium, and lead salts, but apparently not those with mercuric or chromic salts. These compounds are capable of being decomposed by free acids; so that, on the addition of a little sulphuric acid, for instance, to the sodio-ferric salt, the complete ferric pyrophosphate separates.

Allotropic Salts.

Many of these metallic pyrophosphates are capable of existing in a different condition. Thus, the ferric salt already described is very soluble in acids. A few drops of sulphuric acid will dissolve a considerable quantity; but if this solution be heated, it becomes turbid, and a white flocculent salt makes its appearance, which is just like the original ferric compound, but no longer soluble either in pyrophosphate of sodium, ferric chloride, or dilute acids. Like the normal salt, however, it is easily dissolved by ammonia.

Analysis showed that this salt has the same ultimate composition as that from which it is prepared, namely, $P_2fe_4O_7.3H_2O$.

I. 0·377 grm., dried at 100° C., lost 0·065 grm. when strongly heated, and gave 0·277 grm. of pyrophosphate of magnesium.

II. 0·320 grm. gave 0·232 grm. of pyrophosphate of magnesium.

III. 0·255 grm. lost 0·044 grm. when strongly heated.

IV. 0·200 grm. gave 0·071 grm. of ferric oxide.

	Calculated.	Found.			
		I.	II.	III.	IV.
Phosphorus	20·48	20·51	20·24	—	—
Iron	24·65	—	—	—	24·85
Oxygen....	37·03	—	—	—	—
Water	17·84	17·24	—	17·25	—
	100·00				

Other acids may be used in the place of sulphuric acid to effect this change, but free acid is necessary. The normal salt may be boiled with water for a couple of hours without alteration, nor does the presence of neutral salts appear to have any effect. The temperature at which this allotropic salt forms depends upon the comparative amount of the different substances present. If the acid and water be nearly saturated with the ferric compound, a temperature of 30° or 40° C. suffices.

A means of testing for pyrophosphoric acid may be founded on this property. If the presence of that acid be suspected in a neutral solution, it is only necessary to add a drop or two of an iron-salt, sufficient sulphuric acid just to dissolve the precipitate, if any, and boil. The allotropic salt will reveal itself by a cloudiness appearing first in the warmer currents, and then extending itself as a gelatinous or flocculent white precipitate throughout the whole liquid. If it is necessary to employ acid in order to dissolve the substance to be tested, cold sulphuric acid should be employed in as small a quantity as possible.

An allotropic pyrophosphate of copper may be prepared in a way precisely analogous to that given above for the ferric salt. The following analyses confirm its formula as $P_2Cu_4O_7 . 2H_2O$:—

I. 0·407 grm., dried at 100° C., lost 0·044 grm. when strongly heated, and gave 0·193 of oxide of copper, and 0·269 of pyrophosphate of magnesium.

	Calculated.	Found.
Phosphorus.....	18·43	18·45
Copper.....	37·57	37·84
Oxygen	33·29	—
Water	10·71	10·81
	100·00	

Similar precipitates are obtained when solutions of ferrous or zinc pyrophosphate in dilute sulphuric acid are heated, but the lead, chromium, and mercurous salts did not give precipitates under such circumstances.

This allotropism does not seem to extend to pyrophosphoric acid itself, or its compounds, with the alkalis. At least, when the allotropic ferric salt was decomposed by potash, and the allotropic copper salt was decomposed by hydrosulphuric acid, the pyrophosphoric element in solution was found in the normal condition.

Formation and Constitution.

The methods hitherto described for the preparation of pyrophosphoric acid depend on the elimination of water from orthophosphoric acid, or orthophosphates, by means of heat. It may, however, be formed synthetically. If phosphoric anhydride be treated with a solution of hydrate of potassium in absolute alcohol, it forms the pyrophosphate. If oxychloride of phosphorus be dropped into a strong solution of potash, or into a moderately strong solution of ammonia, a violent reaction ensues, and it is a pyrophosphate that is found in solution. If either alkali be too dilute, the orthophosphate is produced; if the ammonia be the strongest, pyrophospho-diamic acid results, as shown in a previous communication.

The formation of a pyrophosphate from phosphoric anhydride and an alkaline hydrate appears very simple:

$$P_2O_5 + 4KHO = P_2K_4O_7 + 2H_2O.$$

It is more difficult to understand how an acid containing P_2 . . . can be produced from the oxychloride, which is PCl_3O, and why the pyrophosphoric amides, which also contain P_2 . . . , should result from the decomposition of the amidated chlorides by water. And this apparent difficulty will be increased when we

come to consider the formation of compounds containing P_4 . . . from the same chlorides. The following considerations may furnish a probable explanation :—

When a chloride and water act on one another, three different courses are open, each giving hydrochloric acid as one of the resultant bodies. In the first case, the chlorine combines with one of the atoms of hydrogen, while the remaining HO (hydroxyl) takes its place in the original compound. Thus :—

$$PCl_3 + 3H_2O = 3HCl + PH_3O_3 \text{ (phosphorous acid).}$$

In the second case, two atoms of chlorine simultaneously attack the two atoms of hydrogen, and the liberated single atom of oxygen takes their place. Thus :—

$$PCl_5 + H_2O = 2HCl + PCl_3O \text{ (oxychloride of phosphorus).}$$

In each of these cases we may consider the new compound as formed on the same type as the original chloride, only in the one case Cl is replaced by HO, and in the other 2Cl are replaced by O:—

$$\text{Thus } P\begin{matrix}Cl\\Cl\\Cl\end{matrix} \text{ becomes } P\begin{matrix}HO\\HO\\HO\end{matrix}$$

$$\text{and } P\begin{matrix}Cl\\Cl\\Cl\end{matrix}\begin{matrix}Cl\\Cl\end{matrix} \text{ becomes } P\begin{matrix}Cl\\Cl\\Cl\end{matrix}O.$$

But there is a third case, where the two atoms of hydrogen in water are attacked simultaneously by two molecules of the chloride, and the result is that the oxygen is left in combination with two molecules of the substance originally combined with the chlorine. Here it is the simplest to consider that it is the water type which is preserved.

It is this third mode of action which explains the production of pyrophosphates from the oxychloride.

If we act on oxychloride of phosphorus with water, we find that a slow replacement of the chlorine takes place, each atom decomposing an atom of water, and the result is

$$P\begin{matrix}Cl\\Cl\\Cl\end{matrix}O + 3H_2O = 3HCl + P\begin{matrix}HO\\HO\\HO\end{matrix}O.$$

which is PH_3O_4, *tribasic or ortho-phosphoric acid*, a body which may be viewed as framed on the same type as the pentachloride.

If, instead of employing pure water in this reaction, we employ a dilute aqueous solution of ammonia or potash, the result is simply a chloride and an orthophosphate.

If, however, we employ these alkaline hydrates in a stronger solution, the result is totally different. We now obtain a salt formed, not on the type of the oxychloride, but on the type of the hydrate, one which we must view as a substitution-product of water rather than of pentachloride of phosphorus. To explain this, the reaction must be broken up into two stages, though it is not improbable that these may occur simultaneously in nature. The first stage is—

$$2PCl_3O + \left.\begin{matrix}K\\H\end{matrix}\right\}O = KCl + HCl + \left.\begin{matrix}PCl_2O\\PCl_2O\end{matrix}\right\}O.$$

and the second is—

$$\left.\begin{matrix}PCl_2O\\PCl_2O\end{matrix}\right\}O + 4\,KHO = 4\,KCl + \left.\begin{matrix}P(HO)_2O\\P(HO)_2O\end{matrix}\right\}O,$$

or $P_2H_4O_7$—*pyrophosphoric acid.*

It thus appears that, according to the strength of the hydrate, either the whole chlorine may be replaced by hydroxyl, or two molecules of the oxychloride of phosphorus may simultaneously attack one molecule of the alkali. There still remains the other possible mode of action, namely, the replacement of two atoms of chlorine by one of oxygen. Thus:—

$$P\begin{matrix}Cl\\Cl\\Cl\end{matrix}O + K_2O = 2KCl + P\begin{matrix}Cl\\O\end{matrix}O,$$

which, acted on by more potash, would give

$$P\begin{matrix}Cl\\O\end{matrix}O + K_2O = KCl + P\begin{matrix}KO\\O\end{matrix}O,$$

or PKO_3—*metaphosphate of potassium;* and this I found to be actually formed when the oxychloride was dropped on oxide of potassium, or on sesquicarbonate of ammonium. At least, there is something produced along with the pyrophosphate which,

when set free by acetic acid, coagulates albumin. Oxychloride of phosphorus does not decompose the dry neutral carbonates of the alkalis, and so metaphosphoric acid cannot be prepared in this way from them.

The production of a pyrophosphate from an orthophosphate by heat would appear to be analogous to the formation of an oxide from a hydrate by the same agency—

$$2CuHO = H_2O + Cu_2O,$$

and similarly,

$$2PNa_2HO_4 = H_2O + P_2Na_4O_7.$$

An argument in favour of $\left.\begin{matrix}P(HO)_2O\\P(HO)_2O\end{matrix}\right\}O$, or $P_2(HO)_4O_3$, as the rational formula of pyrophosphoric acid, may be drawn from the readiness with which it forms amides, since HO and NH_2 are easily replaceable. The fuller consideration of these bodies must, however, be left for another communication.

XLI.—*On Julin's Chloride of Carbon.*

By Henry Bassett.

In the Zeitschrift of the early part of 1864, Dr. Hugo Müller described a substance obtained by the action of pentachloride of antimony on benzol, having for its formula C_6Cl_6, that is to say, perchlorinated benzol. He then suggested the probability that Julin's chloride of carbon had the same rational formula; while Berthelot has ascribed to it the less probable formula, $C_{10}Cl_{10}$, apparently from having obtained naphthalene from it by the action of hydrogen at a red heat; but owing to the known production of napthalene at high temperatures from lower hydrocarbons, this fact could not be considered conclusive.

I have recently made some experiments with Julin's chloride of carbon, which show that it is really C_6Cl_6.

The substance was prepared by passing chloroform vapour

through a long tube filled with broken porcelain, and kept at a bright red heat. The resulting semi-solid product was evaporated to dryness on the water-bath, then boiled with some rather dilute alcohol, and the remainder crystallised once from a mixture of benzol and alcohol. The product has a brownish colour, which is not removed by repeated crystallisation, but by sublimation it is obtained perfectly white, and a subsequent recrystallisation renders it quite pure.

·207 grm. ignited with lime, &c., gave ·63 grm. chloride of silver, corresponding to 75·26 per cent. chlorine, the theoretical percentage being 74·74. The substance thus obtained is only slightly soluble in alcohol, very soluble in benzol and chloroform. It is best crystallised from a hot mixture of benzol and alcohol, from which it separates on cooling in fine long colourless needles, tasteless and inodorous. It volatilizes slightly at 100°, and then has a very faint peculiar smell. It is unaffected by boiling acids or alkalies, permanganate of potash, &c., &c.

Through the kindness of Dr. Müller I have been enabled to compare a specimen of his benzol-derivative with the above, and the two substances are absolutely undistinguishable one from the other. They both fuse at 231° (corrected) and solidify again at 226°.

A determination of the vapour-density of the substance obtained from chloroform was made; owing to its high boiling point (above 300°) it was necessary to heat the flask in an atmosphere of mercury vapour.

Excess of weight of flask	·3535 grm.
Temperature of vapour	350°
Temperature of air	17°
Pressure.....	760 mm.
Capacity of flask.....	79·3 c. c.
Residual air	·6 c. c.

The vapour-density calculated from these data is 10·06, the theoretical value for C_6Cl_6 being 9·87, numbers agreeing sufficiently to show that the body known as Julin's chloride of carbon must be represented by this formula.

XLII.—*Water Analysis; Determination of the Nitrogenous Organic Matter.*

By J. Alfred Wanklyn, E. T. Chapman, and Miles H. Smith.*

It appears to us that the processes employed in water analysis have never been properly investigated; for example, we are unacquainted with a single published experiment on a very important question, viz., the action of water and heat on the organic constituents of sewage. Yet the organic matters specially needing investigation in drinking waters, are in great part derived from sewage. Again, urea must form an important part of the nitrogenous organic matter in sewage; still little or nothing is known of the action of various re-agents employed in a water analysis upon this substance. It has never been proved that the ordinary method of taking the residue of a water yields the same percentage amount independently of the volume of water employed. Now, as it is proved below, certain forms of organic matter undergo alteration when they are heated with water, and this alteration is so slow that in all probability the organic matter contained in the first portion of water poured into the evaporating dish, in the ordinary process of taking the residue of a water, is not completely decomposed even at the end of the operation. From this it follows that if we employ a large volume of water, and occupy therefore a long time in its evaporation, we shall obtain relatively less of the decomposible organic matter, than if we employ a small volume of water and evaporate it rapidly. That this is not an over-refinement is proved by the fact, that a gramme of urea evaporated with quantities of water varying from a litre to 50 c.c., may be made to yield a residue varying from ·98 to ·007; the latter number was obtained by placing a gramme of urea in the platinum dish, and evaporating down a litre of water on it. The evaporation was carried on very slowly. 1 grm. of urea dissolved in half a litre of water, and the solution evaporated to dryness in the water-bath, gave rather under ·7 of solid residue. Evaporated with 50 c.c. of water, 1 grm. of urea gave the number above quoted, viz., ·98. The evaporation was conducted over

* Read June 20th, 1867.

the naked flame, and finished in the water-bath. Indeed we have generally noticed that a somewhat larger residue is obtained by evaporating over the naked flame, than when the evaporation is conducted in the water-bath. We need hardly add that proper precautions to avoid spirting must be taken. We cannot assent to the opinion expressed by Professor Miller in his "Observations on some points in the Analysis of Potable Waters." He there says, "I believe that much would be gained both in precision, and in the comparability of our results, by performing every detail in exactly the same way time after time, as in the common methods of assaying." Such a course of proceeding would certainly give us constant results, and would with equal certainty prevent us from ever obtaining a knowledge of the degree of precision of our processes. A bad water was artificially prepared by diluting 100 c.c. of urine to the volume of a litre. 200 c.c. of this water was evaporated to dryness; the residue weighed ·1644 grm. 100 c.c. centimetres of the same mixture, diluted with an equal volume of distilled water, and evaporated to dryness in the same manner gave ·0750. Now, in this instance, the exact degree of badness was known in each case, and stood in the very simple proportion of 2 to 1. The evaporations in both instances were conducted in precisely the same manner, and very slowly. The figures representing the residue of the waters were as 2 to 1. The numbers actually obtained were as 2 to ·91.

With regard to the determination of ammonia, it has been recently shown by one of us,* that many forms of nitrogenous organic matter yield ammonia when distilled with an alkali, and, as will be seen further on, this fact has been turned to account as a method of determining the degree of badness of a water. But from this it follows that no determination of ammonia in a water by the method ordinarily employed is of any value, because we do not know how much of the ammonia is generated from organic matter during the boiling.

One of us, in conjunction with Dr. Robert Schenk, has shown the utter untrustworthiness of the determination of nitric acid by Pugh's method.

Our results may be summed up as follows:—

1st. That in waters containing much organic matter, the

* "The Laboratory," vol. I, page 114.—(M. H. Smith.)

amount of residue will vary with the length of time that the evaporation lasts, being *largest* when the time occupied is *least.*

2nd. That the percentage amount of residue will vary with the volumes employed in its determination, being *largest* when these are *least.*

3rd. Taking equal volumes of different waters, each containing known but different amounts of organic impurity, the ratio known to exist between the amounts of impurity will not be found to exist in the residue.

4th. That the estimation of ammonia cannot be made in waters containing nitrogenous organic matters by any process involving boiling with an alkali.

5th. That the ordinary method of estimating nitric acid is valueless in its present form.

The following remarks from Hofmann and Blyth's report* have an important bearing on this subject:—

"The organic matter in water has been divided into *nitrogenous* and *non-nitrogenous* matter; but all we know is that certain varieties of the organic matter found in water, contain nitrogen, which is readily shown by treating them with hydrate of potash, when abundance of ammonia is evolved . . . . . And hence the very general and correct opinion that the deleterious character of organic matter in water is proportionate to the amount of *nitrogen* which it contains. Could this nitrogen be estimated with any degree of accuracy, such an estimate would certainly afford the most satisfactory element in the examination of organic matter. Unfortunately this estimate is attended with very considerable difficulties. The nitrogen of the organic matter which has undergone putrefaction, and has therefore ceased to be deleterious, remains in the water partly as ammonia, partly as nitric acid. It would therefore by no means be sufficient to evaporate the water and to determine the amount of nitrogen in the residue. It would be absolutely necessary to estimate also the nitrogen present in the form of nitric acid and of ammonia, and only after the deduction of their joint amount from the total amount, numbers would be obtained, which, representing the quantity of still putrescible nitrogenous substances, would afford, within certain limits, the necessary data for a comparison of the organic matter present in different waters."

* Hofmann and Blyth, "Report to the Board of Health, 1856."

"It is obvious that this mode of proceeding is very complicated, and not likely to furnish trustworthy results, unless carried out with the greatest circumspection, and with all the appliances which the modern progress of analytical chemistry can suggest."

The peculiar feature in our method of dealing with the organic matters present in waters, is to estimate the amount of nitrogenous organic matter by the amount of ammonia which is actually formed during distillation with carbonate of soda, caustic potash, and permanganate of potash.

Direct experiments in which a known quantity of urea, gelatin, and albumin were taken, have shown that all the nitrogen present in these substances is obtainable in the form of ammonia when they are subjected to the treatment about to be described, and has disclosed the very singular fact that boiling with a caustic alkali liberates one-third of the nitrogen, both of albumin and of gelatin, in the form of ammonia, and that a subsequent boiling with permanganate of potash liberates the other two-thirds.

This property may be taken advantage of as a test of albuminoïd matter.

The nitrogen of urea is easily obtainable in the shape of ammonia by boiling with carbonate of soda, whilst albumin and gelatin require a caustic alkali to determine the evolution of ammonia.

Thus we have tests to distinguish between the urea and the albuminoïd matters present in waters.

Further, as the amounts of ammonia given off under each part of the treatment about to be described, can be measured with the greatest ease, we can render the method strictly quantitative.

The following is the method of examination which we employ:—

When possible we determine the ammonia in the water by Nessler's test without *previously distilling*. This may always be effected in waters which have very little colour, and contain more than the very smallest traces of ammonia: for example, in most of the London well-waters. This determination is effected much in the manner described by Prof. Miller in the paper before alluded to, the only difference being that we operate on much larger volumes of water, and employ long,

narrow glass cylinders to enable slight colorations to be better seen.

I. A litre of the water is placed in a retort, carbonate of soda added (about 2 grammes is a convenient quantity to add) and the contents of the retort are distilled rapidly, the distillate being received in a 100 c.c. flask. As soon as the flask is full, it is emptied into a narrow glass cylinder, and at once replaced to be refilled. Nessler's test is now added to the contents of the cylinder. Another cylinder is filled and treated in the same manner, and the operation repeated until no more ammonia can be detected in the distillate. Unless we have an unusually large quantity of ammonia, or urea be present, no ammonia can be detected after the third 100 c.c. have come over. We may now mix the distillates and determine how much ammonia the colour of the mixture corresponds to. The colour lasts quite long enough to allow this to be done without danger of error The ammonia so found, is ammonia existing in the water in the free state, or as salts, and also that derived from the decomposition of any urea that the water contained. If we have been able to determine the ammonia in the water itself, the difference between this and the quantity found by the last process, gives us at once the amount due to the urea, and thence the amount of urea. If we have not been able to make this determination, we can still form some judgment on this subject by noting in which fractions the ammonia came over. Even when urea is present, the first fraction generally contains most ammonia, but the decrease is not nearly so rapid as when no urea is present; of course when the ammonia present as such in the original water admits of being directly estimated before distilling, there is no occasion for this division into fractions, and we may at once distil over 300 or 500 c.c., according to circumstances, and estimate the ammonia in this distillate.

II. The distillation being interrupted, 20 c.c. of a solution of caustic potash (this solution is made by dissolving 100 grm. of potash in 100 grm. of water) are added to the contents of the retort, and the distillation proceeded with. The distillate is, as before, divided into 100 c.c. portions, or preferably collected into one large 300 c.c. portion and submitted to Nessler's test for ammonia.

III. Crystals of permanganate (about 0·3 grm. or more) are next added in such quantity as to render the contents of the

retort of a deep violet colour, and the distillation is proceeded with. It is sometimes necessary to replenish the retort with some 100 c.c. or 200 c.c. of pure (*i. e.* non-ammoniacal) water. This replenishment is necessary where 500 c.c. instead of 300 c.c. of distillate are taken for operation I. The distillation is then resumed, and is generally rather turbulent, and 300 c.c. of distillate are taken over.

The 300 c.c. of distillate is divided into two equal portions, each of which is subjected to Nessler's test.

Distillate I. contains the ammonia originally present in the water, also the ammonia derived from the destruction of urea and allied compounds.

Distillate II. contains less than one-third of the ammonia derived from the destruction of the albumin or albuminoïd substances of the water. A full third of the nitrogen of these substances may be obtained by pushing the potash-treatment to dryness, but in practice, this is inconvenient.

Distillate III. contains two-thirds (and usually much more) of the ammonia derived from albumin and albuminoïd matters.

Qualitative Examples.

Distilled water made in the laboratory of the London Institution, being the first runnings, and hence ammoniacal.

Distillate I. 1st. 100 c.c., pale sherry colour.
2nd. 100 c.c., colour of pale hock.
3rd. 100 c.c., all but colourless.

Distillate II. 1st. 100 c.c., colourless.
2nd. 100 c.c., colourless.
3rd. 100 c.c., colourless.

Distillate III. Colourless.

Water from a pump in Bishopsgate Street, nearly opposite Liverpool Street:—

Distillate I. 1st. 100 c.c. gave even a precipitate with the Nessler's test.

Distillate I. 2nd. 100 c.c. } all much coloured, but last
3rd. 100 c.c. } one much paler than the
4th. 100 c.c. } others.
5th. 100 c.c., very light.
6th. 100 c.c., without colour.

Distillate II. Very light colour.

Distillate III. Decidedly deeper than the last, showing that the water was very ammoniacal, and also contained organic nitrogenous matter.

Water from Berkeley Square :—

Distillate I. 1st. 50 c.c., pale sherry.
2nd. 50 c.c., pale yellow.
3rd. 50 c.c., almost without colour.
4th. 50 c.c., quite colourless.

Distillate II. Coloured, almost without colour.

Distillate III. Coloured deeper, but still faint. This water, therefore, contains next to no urea, and next to no albuminoïd matter.

Quantitative Examples.

Water from the Thames, mid-stream at London Bridge, tide, two hours flood, taken and examined on June 18th. It was filtered before examination.

Quantity of ammonia in a litre of the original water = 1·4 milligrm. NH_3.

Distillate I. 1st. 100 c.c. = 1·4 milligrm., NH_3.
2nd. 100 c.c. = 0·28 „ „
3rd. 100 c.c. = 0·08 „ „
4th. 100 c.c. = traces.
5th. 100 c.c. = absent.

1·76 milligrm., NH_3.

Distillate II. 1st. 100 c.c. = 0·02 milligrm., NH_3.
2nd. 100 c.c. = trace.

Distillate III. 1st. 100 c.c. = 0·28 NH_3.
2nd. 100 c.c. = 0·05 „

0·35 NH_3.

Result: NH_3 existent in the form of urea = 0·36 milligrm.
" " Albuminoïd form = 0·35 "

which corresponds to 1·27 milligrm. of urea, and to 12·6 milligrm. of white of egg, as it exists in a fresh egg.

Thames water, high tide, June 18th, taken at London Bridge, and examined immediately:—

Distillate I. 400 c.c. distilled off; contained much ammonia which we did not determine.

Distillate II.	1st.	100 c.c. gave	·05	milligrm. NH_3.
	2nd.	100 c.c. "	·02	"
Distillate III.	1st.	100 c.c. "	·41	"
	2nd.	100 c.c. "	·07	"
	3rd.	100 c.c. "	·04	"
			·59	

Same sample ½ litre.

Distillate I. 200 c.c. contained 1·02 milligrm. NH_3.
Distillate II. 100 c.c. contained ·04 "
Distillate III. 1st. 100 c.c. " ·20 "

After adding pure water:—

2nd. 100 c.c. " ·04 "
·28

Same sample examined next day, ½ litre. The examination was made by evaporating ½ litre down to 250 c.c. with carbonate of soda, and then digested in a stoppered bottle in the water-bath for three hours, with potash and permanganate of potash, and then put into a retort and distilled.

Distillate = 150 c.c. contained ·25 milligrm. of NH_3.

The three determinations of the same water gave—

·59 milligrm. of NH_3 per litre.
·56 " " "
·50 " " "

The slight deficit in the third determination is most probably

due to the water having been kept a day, and shows the necessity of making these examinations on recent specimens.

The *original* NH_3 (*i.e.* NH_3 existent as such) was 1·85 milligrm. per litre in the fresh water, and in the water after a day's keeping it was 2·00. This confirms what has just been stated about the effect of keeping.

We give next an examination of New River water. The water was taken direct from the main, and examined the same day.

Distillate I. 300 c.c. gave ·06 of milligrm. NH_3.
Distillate II. 300 c.c. „ ·03 „
Distillate III. 300 c.c. „ ·06 „

East London water, which had been kept 18 hours :—

Distillate I. 300 c.c. gave ·01
Distillate II. 300 c.c. „ ·01
Distillate III. 300 c.c. „ ·089

Water taken from a street main, and examined immediately (Southwark and Vauxhall).

Distillate I. 1st. 100 c.c. gave ·015
2nd. 100 c.c. „ ·022
3rd. 100 c.c. „ ·010
·047

Distillate II. 200 c.c. gave ·066
Distillate III. 300 c.c. „ ·140
·206

Postscript August 26th.

The following table shows that albuminoïd ammonia is very frequently found in waters. Bala Lake, and the River Thames near Hampton Court, at the spot where the Water Companies draw off the water, contain about equal quantities of it. The very elaborate filtration effected by some of the Water Companies, diminishes the albuminoïd matter very much, as is apparent on comparing (6) and (7). Surface water is often rich in albuminoïd matter: vide (9), the pump in Bishopsgate-street. Deep springs are sometimes absolutely free from the albuminoïd matter: vide (1) and (2).

Table giving the *Free Ammonia* and *Albuminoïd Ammonia* contained in different waters recently examined.

Date of Collection 1867.	Description of Water.	Parts in 1,000,000, *i.e.*, milligrammes in the litre.	
		Ammonia as such and as Urea.	Albuminoïd Ammonia.
June 24	(1) Water from Cold Harbour, Dorking	0·015	0·00
„ 25	(2) Caterham Water, after Clarke's process	0·040	0·00
July 15	(3) Water from Bala Lake	0·01	0·25
June 26	(4) Loch Katrine, from main in Glasgow	0·02	0·13
Aug. 19	(5) Woodhead Water, supplied to Manchester	0·01	0·07
July 19	(6) Thames, near Hampton Court, unfiltered	0·015	0·23
„ 16	(7) Thames Water, supplied to London, by the West Middlesex Company	0·01	0·064
„ 12	(8) New River Water, London Institution	0·01	0·05
June 28	(9) Pump in Bishopsgate-street, opposite Houndsditch	7·50	0·255
„ 22	(10) Wolsey's Well, Wimbledon-common	0·03	0·159
„ 21	(11) Southwark and Vauxhall Company's Water at London-bridge	0·04	0·20
July 18	(12) Southwark and Vauxhall Company's Water at London-bridge	0·015	0·12

London Institution.

XLIII.—*Analysis of a Biliary Concretion; and on a New Method of preparing Biliverdin.*

By Dr. T. L. Phipson, F.C.S., &c., Member of the Chemical Society of Paris.

The nature and composition of the various products contained in bile, or resulting from its decomposition, have, during the last twenty-five years, given rise to so much discussion, that any facts which may help to throw light on this subject cannot fail, I believe, to be serviceable to science. I have, therefore, the honour of communicating to the Chemical Society the present account of the properties and analysis of a peculiar biliary concretion, as an introduction to an investigation of biliverdin with which I am now occupied.

This concretion was extracted from the liver of a pig a few months ago by Mr. James Forrest, F.C.S., who kindly forwarded the specimen to me for examination. It was of considerable size, being about three inches in length, and two inches wide, and was entirely surrounded by a thin membrane, which isolated it from the tissue of the liver. Its substance is heavier than water, and has a compact structure, without any trace of crystallisation, more or less concentric, of a waxy appearance, and of a yellowish colour, which is neither bright nor uniform, until the substance is pulverised, when it appears as a brilliant yellow powder, similar to chromate of lead. This powder was found to be very slightly acid to blue litmus paper, and very little acted upon by water, alcohol, ether, benzol, and various other solvents, hot or cold. It is not volatile without decomposition, but melts and swells up, and afterwards takes fire, burning with a long fuliginous flame, *exhaling an odour identical with that which is produced in the same circumstances by certain resins, or when common varnish is burnt.* Concentrated sulphuric acid colours it first red and crimson, and then dissolves it with a magnificent emerald-green colour. From this solution water precipitated a green resinous substance, which was found to be biliverdin. Ether extracted from the substance of the concretion a little grease and some cholesterin,

which was identified after being crystallised from boiling alcohol, which yielded it on cooling in its characteristic pearly lamellæ, taking a fine purple colour with concentrated sulphuric acid. After the action of ether, alcohol extracted a notable amount of hyocholate of soda, together with a little free hyocholic acid, and a neutral white substance, which is neither soluble in water, acids, nor alkalis (hyocholin). The hyocholate of soda is isolated from this mixture by water, and upon evaporation the salt is obtained with its characteristic bitter taste, exceedingly permanent; and the free hyocholic acid is next obtained by a dilute solution of soda, when the third substance, which I call hyocholin, remains on the filter. The hyocholate of soda being decomposed by dilute sulphuric acid, yields the acid, which melts readily in hot water below 100° C, and I find that when hyocholic acid is thus melted it is no longer easily soluble in dilute ammonia.

When the calculus is treated with a hot solution of soda for a little time, a large amount of the yellow colouring matter is dissolved, and with it some caprylic acid, easily recognizable by its peculiar odour when the base is saturated with sulphuric acid, as well as by the odour of pine apple, which it gives on being digested with alcohol and hydrochloric acid. The greater portion of the concretion is formed of cholepyrrhin (or biliphein of Heintz) and mucus. The separation of these two substances can only be effected accurately by the following method:—

After determining the moisture at 105° C, the substance of the concretion is left in ether for 24 hours. The ether is then separated, and a new quantity added. In a day or two this is added to the former quantity, and the whole evaporated yields the cholesterin with a small amount of grease. The concretion is then treated several times with alcohol below boiling point, and the liquids being united and evaporated give the hyocholate of soda, with which is mixed some free hyocholic acid and the neutral substance (in appearance somewhat like palmitic acid) before alluded to. If sufficient ether and sufficient alcohol are used, and the whole is left for two or three days, a second treatment with these reagents is not necessary, provided the residue is washed with ether and alcohol. The calculus, being deprived of the substances soluble in these liquids, is next digested with alcohol strongly acidulated with hydro-

chloric acid, and the whole abandoned for a few days. The liquid soon becomes of a bright emerald-green colour, and the colouring matter is entirely dissolved as biliverdin, leaving the mucus, which can easily be separated by filtration. The green solution becomes more and more blue before the whole of the colouring matter is dissolved. When the liquid has become blueish-green it may be filtered, and the mucus washed with dilute alcohol previously acidulated. When water is added to the filtrate, biliverdin is precipitated as a pale bluish-green matter, but in so fine a state of division that it easily passes through a filter. The amount of biliverdin cannot be so well determined in this manner as by another method, to which I will allude presently, which may also serve to prepare biliverdin in large quantities; but it is the only way to determine the amount of mucus.

There is a considerable quantity of chloride of sodium present in the concretion, and also phosphate of lime, but *no trace of taurocholic acid or any other sulphur-compound could be detected in it.* Before proceeding further, the results of the analysis of this concretion may be stated thus:—

	I.	II.
Water	8·00	8·10
Cholesterin, with a small amount of grease	1·35	1·85
Mucus	11·50	10·98
Hyocholate of soda, with some hyocholic acid and hyocholine	2·75	2·75
Cholepyrrhin (Biliphein)	61·36	62·67
Carbonate of lime	1·55	
Phosphate of lime	3·25	
Soda	1·11	13·65
Chloride of sodium	7·13	
Caprylic acid, matters not determined, and loss in analysis	2·00	
	100·00	100·00

In its recent state the concretion contains 37 per cent. of water, but when pulverised and exposed to the air, it loses moisture until it contains only 8 per cent.

This kind of biliary concretion is occasionally met with, I believe, in the liver of the ox as well as in that of the pig. The yellow colouring matter, cholepyrrhrin (or biliphein),

which constitutes the principal portion of it, and the splendid green substance, biliverdin, which is obtained from it, are, without doubt, two of the most interesting organic compounds. The first is probably the same substance that exists in the bile, not only of man, but of all animals; and both present several points of resemblance with chlorophyll, or the green matter of leaves, and xanthophyll, or the yellow substance which takes the place of green chlorophyll in autumn. It has been asserted that the vegetable substance, chlorophyll, exists in certain inferior animals, such as *Hydra viridis* and several *infusoria*. It has also been remarked that chlorophyll has many analogies with the colouring matter of the blood, and, on the other hand, that biliverdin resembles chlorophyll, not only in its properties, but also by its composition. These considerations have led me to endeavour to ascertain whether chlorophyll and biliverdin are really identical in composition, and whether it is chlorophyll or biliverdin which has been found in the inferior animals alluded to. The results of this investigation I reserve for another paper. I will only state here that concretions, such as that which forms the subject of this paper, furnish us with a ready means of obtaining biliverdin in considerable quantities, and that the results of my examination of this substance, and of chlorophyll obtained from the ivy, lead me, so far, to the conclusion that biliverdin differs from chlorophyll only by the elements of two equivalents of carbonic acid.

In 1858 I observed (*Comptes rendus de l'Acad. Paris*) that the yellow colouring matter of leaves in autumn changed to a bright emerald-green in concentrated sulphuric acid. The yellow colouring matter of the concretion here described behaves in the same manner, and biliverdin may be easily prepared from it as follows:—The powder is digested in concentrated sulphuric acid at the ordinary temperature until the whole has become a dark emerald-green. It is necessary to add the substance to the acid in small quantities at a time, to avoid a rise of temperature, and to stir the mixture constantly. In a short time the mucus and other matters are destroyed or dissolved, and a dark green fluid is obtained. This is thrown into a large quantity of cold water, when the biliverdin is precipitated. It must be washed by decantation several times, and not upon a paper filter, which it clogs in a little time more or less completely. The product is finally dissolved in alcohol,

which leaves it quite pure on evaporation. If the quantity obtained is small, it is left as a hard green varnish, which will not allow water to permeate through it; it is quite devoid of crystallisation.

The substance designated as hyocholin, to which I may refer later, resembles palmitic acid, in some respects, but it does not dissolve in dilute alkalis, nor does it float upon water. It amounts to less than 1 per cent. of the concretion.

The mucus obtained as above has, when dry, the appearance of horn. It decrepitates and melts when heated, burning with an odour of burnt feathers. It swells up considerably in water when separated by soda, but alcohol deprives it of this property. Thus, when the concretion is boiled with soda-solution, some of the yellow colouring matter is dissolved, and so is a portion of the mucus, but the latter separates after a certain time, forming a voluminous jelly, which cannot be separated by filtration.

The solution of the cholepyrrhin in soda is bright yellow. When boiled for some time in contact with the air, it becomes green, and acids then precipitate from it *biliverdin mixed with mucus.*

The biliverdin prepared by concentrated sulphuric acid, as already described, dissolves entirely in alcohol with a magnificent green colour, which is very permanent. Even sulphurous acid and nascent hydrogen have no action upon it, after being left in contact with them for several hours, or even for days. On the contrary, the yellow substance from which it is derived has a great tendency to turn green, and is even affected by the action of light, which causes it to become much paler, and, in fact, after some time, nearly white. If biliverdin could be obtained in large quantities, it would be a most valuable tinctorial substance, equalled in brilliancy by no green colour hitherto produced.

XLIV.—*On the Observation of the course of Chemical Change.*

By A. Vernon Harcourt, Lee's Reader in Chemistry at Christ Church, Oxford.

[The substance of a discourse delivered to the Members of the Chemical Society, on June 7, 1866.]

Every change that we can observe may be regarded as presenting to us two problems, the one relating to the manner or course of the change, and the other to its result. But in many cases it is not possible directly to observe both of these. Cosmical changes, which are not simply periodic; changes on the surface, or in the climate of our globe; the succession of animal and vegetable species; these, and others, move too slowly for our study. We can watch their course during the time over which our observations or records extend, and draw some inferences as to their tendency; we may even be able to predict their final result, but the result itself we shall never have the opportunity of observing. On the other hand, very rapid changes give us no opportunity of directly observing their course, and seem at first sight to offer nothing but their result for examination. Most of the transformations of matter are of this kind, and accordingly it is the results of these transformations which have first attracted the study of chemists. Indeed the almost indefinitely great number of such transformations supplies so vast and fruitful a field of research, that chemists have been content to hasten on continually from the discovery of the result of one change to the discovery of the result of another, without examining minutely the course of any single change. In the beginnings of chemistry, a qualitative knowledge of the results of chemical changes was deemed sufficient; the advance of the science dates from the introduction of exact quantitative ideas. At present such knowledge as we possess of the course of chemical changes, and of their relations to the conditions under which they occur, is merely qualitative. For example, every one knows that in making hydrogen, more gas is obtained, within certain limits, if the acid be stronger, the temperature higher, the quantity of zinc greater, and the time

during which the action continues longer; but what relation the quantity of gas bears to each of these conditions is at present wholly unknown.

I am acquainted with only two observations of the course of gradual chemical changes, similar to those which I have attempted to make. In the course of their photo-chemical researches,* Professors Bunsen and Roscoe examined the action of bromine upon tartaric acid in a dilute aqueous solution, in order to discover whether an acceleration occurs in the early stages of the action. They appear to have established the fact that such an acceleration does occur, and compare with it the similar phenomena of photo-chemical induction. More recently an elaborate investigation into the synthesis of compound ethers has been published† by M. Berthelot. Bringing together known quantities of an acid and an alcohol, he determined from time to time, after considerable intervals, the amount of residual acid. He shows that the process of etherification takes place more and more slowly as the proportion of ether and water in the liquid increases, until a limit is attained at which the action stops.

The choice of a chemical change whose course it may be possible and instructive to observe, presents great difficulties. That the observation may be possible, the change must proceed slowly, its conditions at any time must be known, and its amount determinable. That the observation may be instructive, the conditions under which the change proceeds must be either fixed during each observation, or vary in but one or two particulars; and the change itself should be simple and not composite, *i.e.*, occurring in more than one stage.

The two changes which Mr. Esson and I have studied, are, first, the reaction of hydrogen oxalate and hydrogen permanganate; and secondly, that of hydrogen iodide and hydrogen dioxide. Both these reactions occur in dilute solutions at a convenient rate at a convenient temperature; in both cases the amount of change can be exactly determined during its course, and all the conditions which affect it can be kept constant or varied at will.

* Phil. Transactions, 1857, p. 399.

† Ann. Ch. Phys. [3], lxv. 385; lxvi. 5.

I. On the Reaction of Hydrogen Permanganate and Hydrogen Oxalate.

The use of hydrogen oxalate in determining the value of a standard solution of potassium permanganate has made chemists familiar with this reaction. Its final result is thus represented :—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

The conditions of this change, which occurs in a very dilute aqueous solution of the several reagents and products, are—(1) the amount of potassium permanganate, (2) the amount of hydrogen sulphate, (3) the amount of hydrogen oxalate, (4) the amount of potassium sulphate, (5) the amount of manganese sulphate, (6) the amount of carbon dioxide,—in a unit-volume of the solution; (7) the number of unit-volumes; (8) the temperature, and (9) the illumination of the solution; (10) the time during which the change proceeds. Of these ten conditions, only two, viz., those numbered 8 and 9, can in the nature of the case remain absolutely constant during the change. But it is possible to make the proportional variations very small, and a very small variation of any of the conditions, and even a considerable variation of some of them, is found not to affect sensibly the amount of change. Thus, in a highly dilute solution the formation of water, which affects, *pro tanto*, all the conditions from 1 to 7 inclusive, is insignificant; and the presence or absence of minute quantities of potassium sulphate and carbon dioxide appears to be equally immaterial. While exposure to direct sunlight very greatly increases the amount of change, the influence of the differences between lesser degrees of illumination which occur during an observation is not perceptible. Of the other conditions, the effect of varying 1, 2, 3, and 5 was made the subject of a series of experiments; the influence of temperature was not examined; and the 7th and 10th conditions did not need examination, the effect of their variation being manifest *à priori*. For in a homogeneous liquid the total amount of change must vary directly with the volume, and under fixed conditions it must vary directly with the time during which the change proceeds.

Since the change itself is a compound event, consisting in the

disappearance of certain substances, and the appearance of certain others in a constant proportion, its amount may be determined by measuring the quantity of any one of the substances that has disappeared or been formed. In this case it is most convenient to measure the quantity of permanganate that has disappeared, which can be done by estimating the amount in solution at the beginning and end of an interval. This estimation can be effected by adding an excess of potassium iodide to the solution, and measuring the liberated iodine with a standard solution of sodium hyposulphite.

A. *Variation of Hydrogen Sulphate.*

The following series of experiments was made in order to discover the variation in the amount of change due to a variation in the quantity of hydrogen sulphate.

TABLE I.

Relative weights of substances employed :—

$$K_2Mn_2O_8,\quad 5H_2C_2O_4,\quad 2MnSO_4,\quad xH_2SO_4,$$

Actual weight of potassium permanganate, ·015 grm.
Volume of solution, 330 c.c.
Temperature, 16° C.
Duration of each experiment, 4 minutes.

Molecules of hydrogen sulphate. x	Percentage of oxidizing residue. y	Percentage of chemical change. $100-y$
2	78·2	21·8
4	64·0	36·0
6	48·9	51·1
8	36·5	63·5
10	28·4	71·6
12	22·6	77·4
14	17·6	82·4
16	14·3	85·7
22	7·7	92·3

The whole amount of permanganate taken in each experiment is represented by 100. It will be seen that the amount

of chemical change occurring within the allotted time increases continually with the quantity of sulphuric acid in the solution, while the effect of successive increments is less and less. This relation is exhibited by the annexed curve (Plate I), in which the quantities of hydrogen sulphate taken are measured along the axis of x, and the ordinates represent the oxidizing residues. The axis of x appears to be an asymptote of the curve. With no amount of hydrogen sulphate would the action come absolutely to an end in four minutes.

B. *Variation of Manganese Sulphate.*

The following series of experiments resembles the preceding, except that in every experiment a constant quantity of hydrogen sulphate was used, while the amount of manganese sulphate was varied.

TABLE II.

Relative weights of substances employed:—

$$K_2Mn_2O_8,\quad 5H_2C_2O_4,\quad 10H_2SO_4,\quad xMnSO_4.$$

Actual weight of potassium permanganate, ·015 grm. Volume of solution, 330 c.c. Temperature, 16° C. Duration of each experiment, 4 minutes.

Molecules of manganese sulphate. x	Percentage of oxidizing residue. y	Percentage of chemical change. $100-y$
0·0	99·2	0·8
0·25	97·2	2·8
0·5	95·3	4·7
0·75	93·9	6·1
1·0	90·3	9·7
1·25	86·4	13·6
1·5	78·4	21·6
1·75	52·3	47·7
2·0	29·9	70·1
2·25	20·6	79·4
2·5	17·1	82·9
2·75	16·0	84·0
3·0	15·4	84·6
4·0	14·9	85·1
5·0	14·7	85·3
10·0	14·2	85·8

The effect of this variation is made apparent by the curve (Plate II), in which the number of molecules of manganese sulphate used in each experiment, is measured along the axis of x.

When no manganese sulphate is taken, hardly any change occurs in the allotted four minutes; with three molecules of the salt more than five-sixths of the permanganate disappears in the same time. The addition of more than three molecules produces little or no further acceleration. Hence at the dilution and temperature of these experiments, hydrogen permanganate (or potassium permanganate and hydrogen sulphate), is almost without action on hydrogen oxalate. It may even be the case that in a liquid containing no trace of any other reducing substance than hydrogen oxalate or of any other manganese compound than permanganate, no change whatever would occur. But if a single molecule be reduced, the manganese salt thus formed would react with a fresh portion of permanganate to form a compound which does act on hydrogen oxalate; the larger quantity of manganese salt thus produced would react in turn with another larger portion of permanganate, and so the change would proceed with ever-increasing velocity until, having reached a maximum, it slackened again as the amount of active substance diminished. The curve representing the course of this change would have a point of contrary flexure, like those which represent the effect of photo-chemical and idio-chemical induction. In this series of experiments the maximum acceleration occurs when the manganese salt bears to the permanganate the proportion of three molecules to one. Both this fact and the change in colour of the solution, as the action proceeds, make it probable that the change occurs in two stages, the first being the reaction of the two manganese compounds according to the equation,

$$H_2Mn_2O_8 + 3MnSO_4 + 2H_2O = 3H_2SO_4 + 5MnO_2,$$

and the second the reduction of manganese dioxide by hydrogen oxalate. In every subsequent experiment, at least three molecules of manganese sulphate were introduced into the solution, that its formation, during the reaction, might be without influence on the result.

C. *Variation of Hydrogen Oxalate.*

The following tables contain the results of two similar series of experiments, in which all other conditions being kept constant, the amount of hydrogen oxalate was varied. In the first, only potassium permanganate, manganese sulphate, and hydrogen oxalate were employed; in the second, a quantity of hydrogen sulphate was added.

Table III.

Relative weights of substances employed:—

$$K_2Mn_2O_8,\ 3MnSO_4,\ xH_2C_2O_4.$$

Actual weight of potassium permanganate, ·015 grm. Volume of solution, 100 c.c. Temperature, 16° C. Duration of each experiment, 3 minutes.

Molecules of hydrogen oxalate. x	Percentage of oxidizing residue. y	Percentage of chemical change. $100-y$
0	100·0	0·0
1	82·2	17·8
2	71·5	28·5
3	64·7	35·3
4	60·2	39·8
5	56·5	43·5
6	57·9	62·1
7	64·3	35·7
8	87·8	12·2
9	92·0	8·0
10	92·4	7·6
11	93·1	6·9
15	93·3	6·7
20	92·6	7·4
30	92·3	7·7
50	88·0	12·0
100	81·8	18·2

TABLE IV.

Relative weights of substances employed:—

$$K_2Mn_2O_8, \quad 3MnSO_4, \quad 15H_2SO_4, \quad xH_2C_2O_4.$$

Actual weight of potassium permanganate, ·015 grm. Volume of solution, 100 c.c. Temperature, 16° C. Duration of each experiment, 3 minutes.

Molecules of hydrogen oxalate. x	Percentage of oxidizing residue. y	Percentage of chemical change. $100-y$
0	100·0	0.0
1	79·5	20·5
2	57·7	42·3
3	37·1	62·9
4	22·2	77·8
5	12·6	87·4
6	8·3	91·7
7	15·2	84·8
8	38·4	61·6
9	73·6	26·4
10	83·0	17·0
11	86·6	13·4
12	88·2	11·8
15	90·3	9·7
20	91·3	8·7
30	91·0	9·0

The results contained in the last table are represented by the curve (Plate III).

It will be seen that in both cases the quantity of permanganate reduced in three minutes, increases with the proportion of hydrogen oxalate up to a certain point; it then diminishes again until another point is reached; after which, further additions of oxalate produce, once more, a very slight acceleration. The first part of this result is readily intelligible. The rate at which the reduction proceeds is greater with a larger amount of the reducing agent. But why does the addition of a still larger amount produce an opposite effect? The explanation is to be found, no doubt, in another circumstance by which this reaction is complicated. When solutions of manganese sulphate and

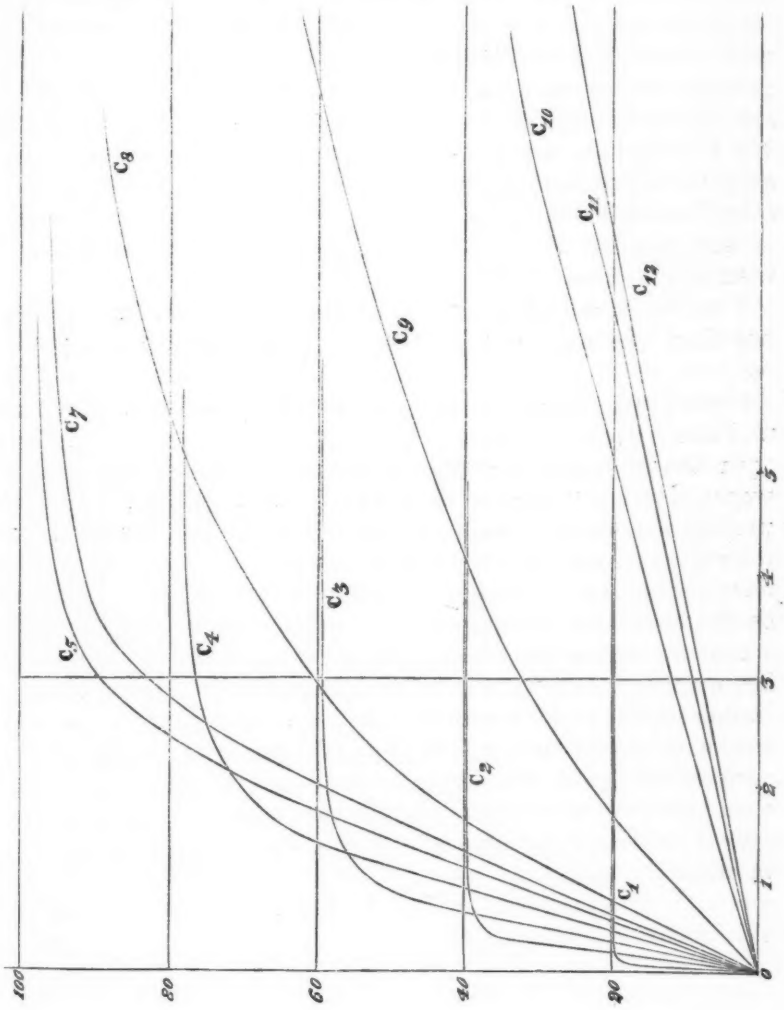
potassium permanganate are mixed, a precipitate of hydrated manganese dioxide is produced, which soon separates from the liquid, leaving it colourless, if the manganous salt were in excess. The presence of a sufficient quantity of hydrogen oxalate prevents this precipitation; a clear, brown liquid is formed, whose colour very slowly fades, the reduction in a cold and dilute solution occupying many hours. This solution, like that of cupric oxide in potash containing a reducing substance, depends, no doubt, upon a chemical combination, which precedes the mutual action of oxidation and reduction. Probably the brown liquid contains manganic oxalate. In the experiments with hydrogen oxalate only, the maximum action in three minutes occurs very near that point at which the amount of oxalate present is five molecules, or the quantity which the measure of permanganate can oxidize. If, as the experiments with manganous sulphate appear to prove, the first stage of the reaction consists in the formation of manganese dioxide, the liquid in which this maximum action occurs, contains one molecule of dioxide and one of hydrogen oxalate. Again, the subsequent minimum nearly coincides with that point at which ten molecules of oxalate have been taken for one of permanganate, or two for one of dioxide. It was also observed, that whenever a less amount than that was taken, the liquid became turbid, but with this or any larger amount it remained clear. According to analogy, manganic oxalate should have the formula $MnO_2,2C_2O_3$, or MnC_4O_8. For its formation two molecules of hydrogen oxalate are required. The final action, when not less than two molecules of hydrogen oxalate have been taken, may therefore be thus represented:—

$$(1) \quad MnO_2 + 2H_2C_2O_4 = 2H_2O + MnC_4O_8.$$
$$(2) \quad MnC_4O_8 = MnC_2O_4 + 2CO_2.$$

The decomposition of manganic oxalate takes place more slowly than does the oxidation of hydrogen oxalate by free manganese dioxide. It is accelerated by the presence of hydrogen sulphate, and, in a much less degree, of hydrogen oxalate.

In the second series of experiments in which hydrogen sulphate was introduced (see Plate III), the amount of action is at first proportional to the amount of oxalate taken, for within the allotted three minutes the whole is oxidized. Afterwards

the total reduction effected within this time is still increased by the addition of a fourth and fifth, and even of a sixth, molecule; but the increase is no longer in direct proportion, but in a less ratio. The explanation already suggested appears to be in accordance with all the phenomena, both of this and of the first series. The rate at which a given amount of oxalate is oxidized diminishes as the total amount present increases up to that point at which enough has been added to convert the potassium



permanganate and manganese sulphate into manganic oxalate and a potassium salt. With one molecule the rate at which its oxidation proceeds is very great; but when it is complete, the percentage of chemical change cannot exceed twenty. Accordingly, it attains this limit in the second series, and nearly approaches it in the first. With two molecules the rate is less, and still less with three, but the proportion oxidized in any time is a less proportion of a larger quantity. When five molecules have been added, the total amount of chemical change possible cannot be increased by a further addition, since this quantity is sufficient to reduce the whole of the permanganate. Consequently, the amount oxidized in any time is thenceforward a less proportion of the same quantity. The diagram on page 469, in which the course of each experiment is represented by a separate curve, having for its asymptote a line parallel to the axis of x at a distance representing the total amount of chemical change possible after the lapse of any time, will serve to illustrate the foregoing explanation.

The experimental numbers in the two tables are to be regarded as a series of measurements of the distance of a point on each curve from the axis of x, along an ordinate whose distance from the axis of y represents an interval of three minutes.

Hydrogen sulphate appears to accelerate the reaction in two ways. First it promotes the action of manganese dioxide on hydrogen oxalate; and, secondly, it retards the formation of the comparatively stable compound, which in its absence is at once produced on mixing the three other ingredients. This is shown by the persistency of the red colour of permanganate in a mixture containing a large proportion of hydrogen sulphate. To the first cause is chiefly due the greater rate of change throughout the series recorded in Table IV, and to the second the circumstance that in this series the maximum action occurs with rather more than five molecules, and the subsequent minimum with more than ten. It seems probable that with a great excess of hydrogen sulphate, the rate at which the reduction proceeds would be found to vary directly with the quantity of oxalate, according to the law which appears to exist in other similar cases.

D. *Variation of Permanganate.*

The effect upon the amount of change of varying its conditions has been examined in the three preceding cases by making a number of experiments in which different quantities of some ingredient have been taken at starting, and the amount of change determined after the lapse of a given time. But since the amount of at least one ingredient of the solution must vary materially during the course of each experiment (for it would not be practicable to employ quantities of permanganate so large as that the amount reduced, which is the measurable incident of the change, and requires for its estimation the determination of the original amount and of the residue, should be an insignificant deduction from the whole quantity), it should be possible by studying the course of a single experiment to ascertain the effect of its variation. This may be done by making a series of experiments differing from one another only in the period which is allowed to elapse between starting and stopping the reaction. In the experiments hitherto related, proportional quantities of the different reagents have been employed; but in order to trace the effect of the progressive variation of a condition during the change, it is desirable that, as far as possible, but one condition should vary. This may approximately be accomplished by taking very large quantities of all the reagents except one, so that the diminution they undergo during the change may be inconsiderable. Table V contains the results of one of the numerous series of experiments that were made by Mr. Esson and me (Philosophical Transactions, 1866, p. 206), in order to observe the influence of a variation in the amount of permanganate upon the amount of change. Each series of experiments was performed in the following manner: In the first place, a mixture was made to serve for all the experiments of the series by bringing together, in a large flask, the proper quantity of all the reagents, except the permanganate, and the proper quantity of water. This mixture was exactly divided, by means of a narrow-necked flask marked to hold 190 c.c., among a number of flasks of about 300 c.c. capacity. One of these was taken, and its contents brought to a convenient temperature, usually 16° C. It was then placed in an arrangement for keeping the temperature constant, consisting of an inner and outer casing, supported over a small lamp; the interval between

which was filled with water of the required temperature. The interior of the inner casing was lined with cotton-wool, and it was provided with a lid similarly lined, which could be slipped over the neck of the flask. A delicate thermometer passed into the fluid through a disc of cardboard, by which the flask's mouth was closed. The standard solution of potassium permanganate was contained in a bottle encased in the same manner, and was kept at the same temperature. A clock beating seconds served to measure the duration of the experiments. To start the reaction, a 10 c.c. pipette was charged with the permanganate solution; the flask was removed for a moment from its receptacle, and at the beginning of a minute the liquid in the pipette was allowed to run into it. By shaking round the flask as the liquid entered, the whole was perfectly mixed at the end of about ten seconds. If the temperature had suffered any disturbance, it was raised or lowered by the application of the hand or of a damp cloth. The flask was then replaced, and required but little attention until the time for stopping the reaction approached. To stop the reaction a measure of potassium iodide solution, containing rather more than enough to reduce the permanganate originally taken, was poured into a test-tube; the flask was then removed from its casing, and, at the proper moment, the contents of the test-tube were discharged into it. By a single rapid shake the iodide is diffused through the liquid, and all the molecules of peroxide which have escaped the slow action of hydrogen oxalate are instantaneously reduced, leaving in their stead so many molecules of iodine, which are without action on any ingredient of the solution, and can, therefore, be estimated at leisure. By using a very dilute solution of hyposulphite, and a freshly prepared and filtered solution of starch, the subsequent determination may be performed with a high degree of accuracy. Some of the measured quantities of the mixed solution were always reserved for a repetition of previous experiments; in several instances the whole series was performed twice. The readings of the burette after two similar experiments seldom differed by more than 0·15 cub. centim. From time to time the value of the measure of permanganate was taken in terms of the solution of hyposulphite, and the numbers given as the percentage of residue are obtained by multiplying the actual readings on the burette by 100, and dividing by this number.

TABLE V.

Relative weights of substances employed :—

$$K_2Mn_2O_8,\quad 14MnSO_4,\quad 108H_2C_2O_4.$$

Actual weight of potassium permanganate, ·015 grm.; volume of solution, 200 c.c.; temperature, 16° C.; duration of each experiment, x minutes.

Duration of experiment.	Oxidizing residue.		Duration of experiment.	Oxidizing residue.	
	Found.	Calculated.		Found.	Calculated.
x	y	y	x	y	y
2	94·8	94·8	31	44·0	44·0
5	87·9	87·6	35	39 1	39·6
8	81·3	80·9	44	31 6	31 2
11	74·9	74·7	47	28 3	28 8
14	68·7	69 0	53	24 2	24 6
17	64·0	63 7	61	20 2	19 9
27	49·3	48 9	68	17 0	16 5

This series may be regarded as exhibiting the course of a single experiment in which the change is allowed to proceed during 68 minutes; of a hundred parts of oxidizing substance originally present, there remain after two minutes 94·8 parts, after five minutes 87·9 parts, after eight minutes 81·3 parts, and so on. The curve on Plate IV represents, as it were, the path of the reaction, showing how much oxidizing substance remained, and consequently how much chemical change had taken place, at any moment after the time of starting. The calculated numbers which, it will be seen, agree very fairly with the experimental numbers, are obtained from the equation $y = 100\ (·974)^x$. Thus the amounts of residue after equal times form a series in geometric progression. It can be shown that this relation between the numbers is that which should exist if the amount of change occurring at any moment be proportioned to the oxidizing residue.

This result probably represents a general law of chemistry which may be thus stated: When any substance is undergoing a chemical change, of which no condition varies excepting the diminution of the changing substance, the amount of change

occurring at any moment is directly proportional to the quantity of the substance. In most of the series of experiments made upon this reaction the conditions were, as it now seems, unnecessarily complicated by the employment of hydrogen sulphate as well as hydrogen oxalate. Instead of a single reaction it is probable that, in presence of this acid, the following changes occur:—1. As soon as the solution of potassium permanganate is added to the liquid containing an excess of hydrogen oxalate and manganous sulphate, manganic oxalate is formed. Unless the quantity of hydrogen sulphate be very large, this change occurs almost instantaneously, and therefore does not affect the course of the change. 2. Manganous sulphate and manganic oxalate react to form manganous-manganic oxalate or sulphate. It is this reaction which appears to be determined by the presence of hydrogen sulphate; and through its occurrence we find under our observation three changes instead of one. 3. Manganic oxalate is decomposed. 4. Manganous-manganic oxalate or sulphate is decomposed, or reduced by hydrogen oxalate.

The last three changes are all gradual, and consequently the numbers which express the amounts of residue, or of chemical change at different times during the course of the change are not related one to another as in the former case.

But these numbers are always consistent with the hypothesis that each of the three changes which thus occur simultaneously obeys the law stated above.

In some earlier experiments upon the course of this reaction, instead of the reducing agent being employed in great excess over the oxidizing agent, the two were employed in the proportions in which they act one upon another. The first indication of the law of proportionality was obtained from these experiments; for it was observed that the product of the numbers representing the duration of an experiment and the amount of residue was, for many consecutive experiments, a constant quantity. Or, regarding the series of experiments as exhibiting the course of the change, it appeared that for a great part of its course the residues were inversely proportional to the duration of the action. From this it follows that the amount of change occurring at any moment varies as the square of the amount of the changing substance whose residue is measured. But in this case two substances disappear simul-

taneously, and they are present in proportional quantities, so that for any fraction of the total amount of change the same fraction of each of these substances disappears; whence the product of the amounts of the two at any time is equal to the square of the amount of one. And hence the amount of change occurring at any time varies as the product of the amounts of these two substances, that is to say, as the amount of each of them.

However, none of the series of experiments made with proportional quantities of potassium permanganate, and hydrogen oxalate exhibits throughout this simple relation between the duration of the action and the amount of residue. The departures from it are undoubtedly due to the simultaneous occurrence of more than one gradual change.

It became more and more evident during the course of these experiments that the case of chemical change under investigation had not the simplicity which is needed if any interpretable results are to be obtained from the systematic variation of its conditions. To estimate the effect, for example, of a variation of temperature, it is absolutely necessary that we should only have to deal with the rate of change of a known quantity of a single substance. Even if at one temperature the action appeared to be accomplished in a single stage, it might well be the case that at another it would take place in several stages, and that the final measurement might be of the mixed residues of various reagents, each formed and reduced at a different rate. The likelihood of such a complexity appears to be greater where the change consists in the removal of several atoms, not forming a transferable group, from a single molecule. And although for the investigation of the course of a change it is not necessary that it should be the only change occurring, but merely that it should be the only gradual change, so that its rate may be independent of other changes; yet even this degree of simplicity is less likely to be attained where, as with the reduction of permanganate, several substances exist intermediate between the original substance and the final product of the change.

These considerations led me to seek for a case of chemical change which should satisfy the condition of simplicity as well as the other conditions which must be satisfied in order that the observation of its course may be possible. After trying many reactions, I observed that when hydrogen dioxide and iodide

are mixed in an acid solution, the colour of iodine is gradually developed, and that when this colour is removed by the addition of a small excess of hyposulphite, it presently reappears. On this observation a method was founded for investigating the reaction of these two substances.

II.—On the Reaction of Hydrogen Dioxide and Hydrogen Iodide.

The equation representing this reaction is $H_2O_2 + 2HI = 2H_2O + I_2$. The principle of the method of investigation consists in the addition to a solution containing hydrogen dioxide, hydrogen iodide, and a little starch, of successive portions of sodium hyposulphite. Not only is the iodine which may have been formed in the solution instantly reconverted into iodide by this reagent, but the iodine which is continually being liberated is at once recombined, so that the liquid, though it contain starch, and though iodine is being formed in it, rests quite colourless, as long as any hyposulphite remains. But when the last trace of hyposulphite has been changed into tetrathionate by the action of the iodine, the portion of iodine next formed remains free, and the liquid becomes suddenly blue. The addition of another small portion of hyposulphite again removes the colour; till all the hyposulphite has been destroyed it remains colourless, and then the blue colour re-appears. In a dilute solution containing iodide, hyposulphite is neither decomposed into sulphur and sulphite by the action of hydrogen sulphate or chloride, nor is it oxidized to sulphate or in any way acted upon directly by hydrogen dioxide.

The apparatus employed in these experiments consisted of a glass cylinder about 12 inches high and 3 broad, round which, within $2\frac{1}{2}$ inches of the top, a fine line was etched; into the cylinder, through a bung closing its mouth, passed a thermometer and an inverted funnel tube; the latter, which occupied the axis of the cylinder, and reached nearly to the bottom, was connected with an apparatus for generating carbon dioxide; a third hole in the bung, which served to give access to the contents of the cylinder, was ordinarily closed with a small cork.

The method of performing an experiment was as follows:—A quantity of water, purified from organic matter by redistillation off potassium permanganate, was boiled for some time to

expel dissolved oxygen, and then allowed to cool in an atmosphere of carbon dioxide. When cold it was poured into the cylinder which had previously been filled with carbon dioxide, and a current of this gas, ascending in large bubbles from the inverted funnel, was kept passing through the liquid until the close of the experiment. These bubbles of gas, whose diameter is nearly half that of the cylinder, serve the purpose of stirring the fluid constantly, and to any required degree, without causing loss or exposure to the air, and without danger to the thermometer. Measured quantities of the standard solutions were then introduced, and, the liquid having been brought to the proper temperature, the cylinder was placed on a levelling-stand, and so much more water added as would make the upper surface of the fluid exactly coincide with the line etched upon the vessel. In every experiment the same volume of hydrogen dioxide was employed, and thus the total volume after its addition was always the same. Two operations, however, had still to be performed before starting the reaction, by the addition of dioxide. First, it was necessary to make sure that the fluid contained no trace of any oxidizing or reducing substance. To this end the colour of the fluid (which contained some free acid, iodide, and starch) was brought to the faintest possible blue by the addition, according to circumstances, of a trace of hyposulphite or hypochlorite. If, at the end of half an hour, the blue tint had neither deepened nor disappeared, it was considered that the experiment might be proceeded with. Secondly, it was necessary to add a little measure of sodium hyposulphite, the first of a series of similar measures, which were to play the part already indicated in the observation of the course of the reaction. These measures needed to fulfil two somewhat incompatible conditions; they must be very exact, and they must, at the same time, be of very small volume, that their addition might not materially augment the total volume of the fluid. In the earlier experiments a pipette, of about half a cubic centimetre capacity, with a capillary tube at either end, was filled with the hyposulphite by means of a syphon, whose shorter limb dipped into a bottle of the solution, while its longer limb was recurved at its extremity, and terminated in a piece of india-rubber tubing, an inch long, nipped in the middle by a pinch-cock. The lower end of the pipette having been wiped, and pressed gently against a pad of blotting-paper, was inserted

into the cylinder through the hole in the bung, so as to dip beneath the surface of the fluid. By applying the mouth to an india-rubber tube, slipped over the upper end of the pipette, and alternately blowing and sucking, the charge of hyposulphite was driven and completely washed into the great body of fluid within the cylinder. This mode of measurement proved to be susceptible of great accuracy, but where, to make many observations, many pipettefuls had to be added, the increase in the total volume of fluid was not inconsiderable.

Subsequently a method of measurement was devised, by which this source of error was avoided. It consisted in collecting single drops of a strong solution of hyposulphite, under circumstances favourable to their perfect uniformity, and introducing these in succession into the cylinder. The drops were formed at the end of a syphon, of which the shorter limb passed into a bottle containing the standard solution, while the longer limb, clamped firmly to a solid stand, was protected at its extremity by an outer tube, which extended slightly below it, and served to shield the growing drop from currents of air. The syphon was at one point so contracted as to deliver not more than five drops in a minute. The drops were received in small tubes, about six inches long, open at both ends; in the side of each tube, near one extremity, a round hole had been blown such as would be made for the purpose of joining on another tube at right angles. Two forks were so placed on either side of the long limb of the syphon, as that when one of these tubes had been passed through and rested upon them, it lay horizontally, just under the dropping-point, and could easily be so adjusted as to receive a drop through its lateral opening. When a drop had fallen, the tube containing it was withdrawn, and replaced by another tube, until a sufficient number of drops had been collected. An india-rubber cap was then slipped over the dropping-point to stop the flow of the liquid. The whole apparatus remained always in readiness, needing only the removal of its cap whenever it was desired to collect a fresh series of drops. The width of the bottle containing the standard solution is so great, in comparison with the quantity of solution taken for any one set of experiments, that the available length of the syphon and the rate of flow, upon whose constancy that of the drop depends, varies in no appreciable degree. Numerous determinations were made with standard iodine solution of

the values of drops thus collected, and they proved to be perfectly equal. To introduce a drop into the fluid in the cylinder, the end of one of the tubes thus charged was dipped into it and moved up and down, while an active stirring was carried on by means of the bubbles of carbon dioxide.

When, then, the preparations, already described, had been completed and a sufficient number of tubes, each loaded with its drop, were lying in readiness, it remained to add to the contents of the cylinder a measure of hydrogen dioxide, and to mix it as thoroughly and as rapidly as possible with the rest of the fluid. Since, however, the addition and mixing are far from being instantaneous, an experiment was not made to date from this point, but from the moment of the first appearance of the blue colour. In order that the second at which this change occurred might be accurately noted, the cylinder was placed on a sheet of white paper, in a good light, and opposite to it was stationed a clock, beating seconds. The paper lay on an iron plate, one end of which was heated, more or less gently, by a lamp, according to the temperature at which the set of experiments was to be performed, and that of the surrounding air. By moving the cylinder nearer to, or further from the heated end of the plate, the temperature of the fluid could be conveniently regulated. The observations were made by looking down upon the column of fluid and watching the appearance of the disc forming its upper surface, listening, at the same time, to the beat of the clock, and counting the seconds. So suddenly does the blue shade pass over the clear and brightly illuminated disc, that a practised observer can generally feel sure as to the second in which the change begins, and where the reaction is proceeding very rapidly it would often be possible to subdivide the second. As soon as the observation had been made, a drop of hyposulphite was introduced, which speedily restores the liquid to its normal colourless condition.

The time that elapses between two successive appearances of the blue colour becomes continually greater as the amount of dioxide in the solution diminishes; and, finally, the last measure of hyposulphite requires for its conversion more iodine than the residual dioxide can furnish, and the blue colour never returns.

The values of the measure of dioxide and of the drops can be compared by determining each with a standard solution of potassium permanganate. To apply this reagent to the estima-

tion of sodium hyposulphite, it is necessary to add to the solution potassium iodide and hydrogen sulphate, together with a little starch. When added to this mixture permanganate does not act directly on hyposulphite, but sets iodine free, and the iodine acts upon the hyposulphite. The result of the determination is the same as though an acid solution of iodide were first decomposed by a measure of permanganate, and the iodine thus liberated were compared with the measure of hyposulphite. In this determination hydrogen iodide plays, in fact, exactly the same part as it does in the reaction just described, in which hydrogen dioxide is the oxidising agent.

The relation between the measure of dioxide and the drops of hyposulphite may also be determined in another manner. It is possible at the close of the actual set of experiments, having allowed the liquid in the cylinder to stand until the action has come practically to an end, to determine the excess of hyposulphite by means of a standard solution of iodine or permanganate, and then to determine by the same means the value of an entire drop subsequently added. Hence we know what fraction of a drop, in addition to the entire drops previously introduced, has been required to reduce the whole of the dioxide, and this quantity—the whole number and the fraction—expresses the value of the dioxide at the commencement of the experiment. If we call this quantity $n + p$, where n is the number of drops used in the series of experiments, and p is the part of the last drop acted on by the dioxide, then at the moment of the second observation, an amount of dioxide corresponding to one drop having been reduced, the quantity of dioxide in the solution is $n - 1 + p$, and at the moments of subsequent observations it is, successively, $n - 2 + p$, $n - 3 + p$, &c., until finally, at the moment of the last observation, only p remains. Now the decrease of the dioxide is a measure of the amount of chemical change. Each time that the operation represented by $H_2O_2 + 2HI = 2H_2O + I_2$ is performed, a molecule of dioxide disappears. We may therefore regard the change by which $n + p$ parts of dioxide become $n - 1 + p$ parts, as a definite portion of chemical change. Representing, then, the observed times by t_0, t_1, t_2, &c., $t_1 - t_0$, $t_2 - t_1$, &c., are the successive intervals in which, as the experiment proceeds, this portion of chemical change is accomplished. Now, if all the conditions of the reaction could be kept constant, if it were

possible to reconvert the water which is formed into hydrogen dioxide, as well as the iodine which is formed into hydrogen iodide, then, since no condition of the change would vary, the intervals $t_1 - t_0$, $t_2 - t_1$, &c., would be equal. But, as it is, the quantity of hydrogen dioxide in the solution is continually diminishing, and the variation in the length of the intervals $t_1 - t_0$, $t_2 - t_1$, &c., is due solely to the variation of this condition.

A. *Variation of Hydrogen Dioxide.*

The following table contains the results of one of our first sets of experiments. The standard solutions employed in it and in subsequent sets were (1) dilute hydrogen sulphate, containing ·37 grm. in a cub. centim.; (2) a solution of potassium iodide containing ·06 grm. in a cub. centim.; (3) a solution of sodium dioxide containing ·00127 grm. in the same volume. Of the first of these 100 c.c. were taken, and 10 of each of the others. The total volume of the solution was very nearly one litre, and its temperature 17° C. The measures of hyposulphite were such that 21·45 of them were equivalent when determined by permanganate to the measure of sodium dioxide. Before starting the reaction, by adding the solution of dioxide, half a measure of hyposulphite was introduced. At the moment, then, of the first appearance of the blue colour, from which moment the observed times in column 2 date, the amount of dioxide in the solution, measured in drops of hyposulphite, was 20·95. The numbers in column 1 express the quantities of dioxide present in the solution at the observed times, those in column 4, the intervals between two successive observations, and those in column 3, the amounts of chemical change that occurred in those intervals. The relation between the series of numbers in these columns is represented by the curve, Plate V. This curve, which is drawn through 20 experimental points, corresponds to that on Plate IV, which exhibits the course of the reduction of a small quantity of potassium permanganate by an excess of hydrogen oxalate. Along the axis of x is measured the time of each observation, dating from the commencement of the set of experiments, and along the axis of y the amount of dioxide present in the solution at each of the times (Table VI, columns 1 and 2). Through each experimental point

a line is drawn, parallel to the axis of x, to meet a line drawn through the point next below it, parallel to the axis of y. These lines represent the quantities measured in each experiment (columns 3 and 4), namely, the interval between two successive observations, and the amount of chemical change.

TABLE VI.

I.	II.	III.	IV.
Amount of Dioxide.	Time from the beginning.	Chemical change in each interval.	Intervals.
20·95	′ 0·00		′
19 95	4 57	1	4·57
18 95	9 37	1	4 80
17 95	14 5	1	5 13
16 95	19 87	1	5 37
15 95	25 57	1	5 70
14 95	31 68	1	6 11
13 95	38 20	1	6 52
12 95	45 23	1	7 03
11 95	52 82	1	7 59
10 95	61 12	1	8 30
9·95	70 15	1	9 03
8 95	80 08	1	9 93
7 95	91 27	1	11 19
6 95	103 88	1	12 61
5 95	118 50	1	14 62
4 95	135 85	1	17 35
3 95	157 00	1	21 15
2 95	184 53	1	27 53
1 95	223 45	1	38 92
0 95	291 18	1	67 73

If the course of the change observed has been determined by a single gradual reaction, and the law of proportionality holds good, we shall expect to find that the amount of change at any moment has varied directly with the quantity of dioxide in the solution; and if this be the case, the quantities of dioxide at the end of a series of times taken in arithmetical progression will be in geometrical progression, and the curve, as before, a logarithmic curve.

For the method of calculation by which the accordance of the experimental results with this theory is most conveniently tested, I must refer to a statement in the Philosophical Transactions for this year (pp. 123, et seq.) by Mr. Esson, who shows

that the equation applicable to the preceding table, if the theory be correct, is

$$y' = y\, e^{-\alpha(t'-t)}$$

where y and y' are the amounts of dioxide present in the solution at the beginning and end of an interval $t' - t$, α the fraction disappearing in a unit of time, and e the base of Napierian logarithms. This equation may be written in the form, more convenient for calculation,

$$\log.\log.\frac{y}{y'} - \log.(t'-t) = \log.\alpha + \log.\log.e.$$

Each experiment supplies a value for $\log.\alpha + \log.\log.e$; the mean of these values which approximate very closely one to another, is $\bar{3}\cdot664$. Hence the equation for calculating the length of successive intervals is

$$\log.(t'-t) = \log.\log.\frac{y}{y'} - \bar{3}\cdot664.$$

In the following table a series of intervals calculated by this formula is compared with those actually observed.

TABLE VII.

Intervals.		Intervals.	
Observed.	Calculated.	Observed.	Calculated.
′	′	′	′
4·57	4·61	9 03	9 02
4 80	4 84	9·93	9 98
5·13	5 12	11 19	11 14
5 37	5 38	12 61	12 65
5 70	5·71	14 62	14 62
6 11	6 09	17 35	17 30
6 52	6·52	21 15	21 24
7 03	7 00	27 53	27 48
7 59	7 57	38 92	39 00
8 30	8·23	67 73	67 73

These numbers exhibit throughout a very satisfactory agreement. The two which are least accordant, namely, the second and tenth, differ by rather less than one per cent. The greatest

absolute difference amounts to ·09 minute, or between five and six seconds. It is to be remembered also that these deviations ought not to be attributed entirely to errors of observation. They are more probably due to the simultaneous occurrence of different errors in the same direction. For example, it may happen (and in eleven experiments it is an even chance that the case will occur) that the measure of hyposulphite is less than the mean, the temperature of the solution too high, the first observation made too late, and the second observation too soon. All these errors conspire to make the experiment in which they occur occupy too short an interval; and such a divergence as that of the second experiment of this set would be produced if the measure of hyposulphite were a fifth per cent. smaller than usual, the temperature 0°·025 too high, and the observed interval one second too small. None of these errors are such as may not easily occur, whatever care is bestowed on the measurements and observations. Hence we may conclude that within the limits of experimental error the results obtained agree with the theory. The amount of chemical change occurring at any moment is proportional to the amount of dioxide in the solution.

We have made a large number of similar sets of experiments under very various conditions, substituting hydrogen chloride, and hydrogen and sodium carbonate, for hydrogen sulphate, using the reagents in all proportions, varying the temperature from 0° to 50° C., and making the change proceed as slowly and as rapidly as is consistent with accurate observation. Under all these circumstances the reaction still conforms to the same law.

Having thus established the relation existing between the amount of chemical change and the amount of hydrogen dioxide, we can proceed to examine how the amount of change is related to the other conditions of the reaction.

For a particular system the amount of chemical change in a unit of time may be expressed by αy, where y is the amount of dioxide in the solution, and α the fraction of it which disappears in a unit of time. This expression represents the fact that if α is kept constant, the amount of change varies directly with y, as has just been shown, and also that if y is kept constant it varies directly with α. In the sets of experiments upon the variation of y, that which has been kept constant, and

which is represented by α, is a group of other conditions upon which the amount of chemical change depends. These are the amounts of iodide and of hydrogen sulphate or hydrogen chloride (or of other substances that, being introduced, affect the rate, but not the nature, of the reaction) in a unit volume of the solution, the volume of the solution, and its temperature. Besides these there are the two conditions whose relation has been already examined, the amount of dioxide in a unit-volume of the solution, and the time during which the change proceeds. The small quantity of tetrathionate, which is, except water, the only permanent product of the reaction, does not appear to produce any effect.

The whole amount of chemical change is a function of all the conditions of the system in which it occurs. If we call this amount Σ, the volume of the system v, its temperature h, the time during which the change proceeds t, and the number of units of hydrogen dioxide, iodide, &c., in a unit of volume $d, i, \ldots . a, b, c, \ldots \ldots$, respectively, then

$$\Sigma = f\ (a, b, c, d\ .\ .\ h, i, \ldots \ldots t, \ .\ .\ v).$$

The form of this function is determinate in the case of two of these conditions, viz., t, v, and has been determined experimentally in the case of d, so that the equation may be written in the form

$$\Sigma = d\ t\ v\ .\ f\ (a, b, c, \ldots\ h, i, \ldots\ ).$$

Now, if we keep constant all the conditions in the indeterminate part of the function except one, say x, the form of the equation is—

$$\Sigma = d\ t\ v\ .\ \phi\ (x),$$

the constants in $\phi\ (x)$ being functions of the conditions of the system, which do not vary.

In each set of experiments made in the manner described, d and t vary, while v and x remain constant, and the law of connexion between d and t is such that the amount of change within a unit of volume in a unit of time is $\alpha\ d$; hence $\Sigma = \alpha\ d\ t\ v = d\ t\ v\ .\ \phi\ (x)$, and therefore $\alpha = \phi\ (x)$. If we now make a *series* of such sets of experiments, varying x only, and determining the value of α for each set, we shall obtain a series of values of $\phi\ (x)$ corresponding to the several values of x,

and may thence discover what function α, and therefore Σ, is of x; and if we are able thus to determine what function Σ is of each of the conditions $a, b, c, \ldots$, we shall obtain an equation expressing the laws of connexion between all the conditions of the change and its amount.

It is plain that the investigation of a single reaction thus considered is a work requiring the performance of a very large number of experiments. Many substances besides those named may be introduced into the solution without affecting the nature of the reaction, and each of these furnishes a fresh subject of inquiry, namely, as to the effect of a variation in its amount upon that of the chemical change. It will thus be possible to determine quantitatively the effects which are due to the presence of substances which do not themselves undergo any change, and to compare by a new standard of equivalency different chemical substances one with another. The only kind of substance besides dioxide whose presence is essential to the change is iodide. The following results have been obtained by varying its amount in successive sets of experiments:—

B. *Variation of Iodide.*

When two salts are mixed in solution, and no precipitation occurs, or change in the colour of the liquid, it is not possible to arrive at any probable conclusion as to the proportions or nature of the salts which the solution contains. In the greater part of these experiments, potassium or sodium or hydrogen iodide was added to a liquid containing an excess of hydrogen sulphate or chloride. Whether the systems thus formed contained the salts introduced into them, or hydrogen iodide and a metallic sulphate or chloride, or whether the metallic iodides were partially decomposed by the excess of free acid, we are unable to say. It may be hoped that the further investigation of the effect of varying these substances will throw light upon this question; but at present we must consider our results generally as depending upon the variation of iodide. In stating the conditions of a set of experiments, it is convenient, instead of giving the actual weights of the different substances in the solution, to state the amounts in one cub. centim. Indeed, after all the ingredients have been introduced and mixed, the absolute quantities are immaterial; and if it should happen, for

example, that in the course of a set of experiments, the cylinder were upset, and a part of the liquid were lost, the remaining observations would still give a right result. To express the weights entering into one cub. centim. of a very dilute solution most conveniently, I employ the millionth of a gramme as the unit of weight; and in order to convey also at a glance information as to the proportional quantities of the different substances, I propose to represent by the symbol of a substance printed in italics its molecular weight, taken as an absolute quantity, viz., so many millionths of a gramme. Thus H_2 means two millionths of a gramme of hydrogen, *KI* 266 millionths of a gramme of potassium iodide; and the expression

$$H_2O_2 + 2HI = 2H_2O + I_2,$$

represents the disappearance of 34 millionths of a gramme of hydrogen dioxide, and of 256 millionths of a gramme of hydrogen iodide, and the formation of 36 millionths of a gramme of water, and 254 millionths of a gramme of iodine. This amount of change may be called the unit change, and its occurrence in one minute the unit rate.

The sets of experiments of which the results are recorded in the following table differed from one another only in the quantities of potassium iodide taken in each case, and the consequent differences in the rate of change.

Each cubic centimetre of the solutions contained

$$(381{\cdot}3 - 1{\cdot}82z)\ H_2SO_4,\quad 1{\cdot}82\ \{(n - z)\ KI + z\,HI\},$$
$$1{\cdot}82z\ KHSO_4,$$

n (1·82 *KI*), being the weight of potassium iodide taken for every cubic centimetre of the several solutions, and z being the fraction of this iodide decomposed by the hydrogen sulphate.

The quantities of hydrogen dioxide and of sodium hyposulphite at the moment of the introduction of each, by whose relative quantity the number of observations is regulated, was in each case about

$$\cdot224\ H_2O_2 \text{ and } \cdot004\ Na_2S_2O_3.$$

By the side of each observed interval is placed the value for α calculated from it.

TABLE VIII.

$n = 2$.		$n = 3$.	
Intervals.	α	Intervals.	α
′		′	
7·33	·0302	4·78	·0457
9 40	·0302	6·14	·0455
35·47	·0301	8·61	·0452
103·63	·0303	14·39	·0449
		53·26	·0451

$n = 4$.		$n = 5$.		$n = 6$.	
Intervals.	α	Intervals.	α	Intervals.	α
′		′		′	
3·65	·0604	2·87	·0757	2·35	·0923
4·73	·0600	3·68	·0755	3·10	·0895
6 59	·0604	5 12	·0757	4·25	·0906
11·16	·0601	8·55	·0748	7·05	·0900
52·20	·0601	29·78	·0762	23·97	·0902

The values obtained for α from the different experiments of each set are fairly concordant, and we may therefore assume their mean to be the true value. It is at once evident that these numbers are in arithmetical progression, and bear to one another the same ratios as the values of n, viz., 2 : 3 : 4 : 5 : 6. They are compared below with a series of numbers calculated on this hypothesis:—

TABLE IX.

n	α Observed.	α Calculated.
1	.....	·0151
2	·0302	·0302
3	·0453	·0453
4	·0602	·0604
5	·0756	·0755
6	·0905	·0906

To confirm this result, a second series of sets of experiments was made, differing from the former by the substitution of hydrogen chloride for hydrogen sulphate. The mean values of α, derived from these sets of experiments, are compared in the following table, with a series calculated from the equation $\alpha = \cdot01347\ n$.

TABLE X.

n	α Observed.	α Calculated.
1	·0136	·0135
2	·0268	·0269
3	·0404	·0404
4	·0538	·0539
5	·0672	·0673
6	·0804	·0808
7	·0948	·0943
8	·1080	·1078

Thus it appears that the amount of chemical change occurring in the solutions, at any moment, varies directly with the amount of iodide, if all the other conditions are the same.

In both these series, however, the quantity of iodide was small in proportion to the quantity of acid, amounting at the most to 4 per cent. Two sets of experiments made with systems containing in a cubic centimetre 54·5 H_2SO_4, and 10·42, 20·84 KI, respectively, at a temperature of 17° C., gave for the values of α, ·0116 and ·0243, the latter of which is considerably more than double the former. In some other sets of experiments, in which, instead of a metallic iodide, different quantities of hydrogen iodide were added to the solutions, it was observed similarly that the increase in the rate of change was more than proportional to the increase of hydrogen iodide. Now, since it appears that hydrogen sulphate or hydrogen chloride, though playing no immediate part in the reaction, yet accelerates its course, it seems reasonable to suppose that a double effect may be produced by the addition of hydrogen iodide. For while on the one hand this addition increases the amount of substance which the hydrogen dioxide has to act upon, on the other hand, like the addition of hydrogen sulphate or hydrogen chloride, it

increases the acidity of the solution. But further, the rate of change depends, not only upon the acidity of the solution, but upon the particular acid which it contains. Hydrogen chloride exercises a much greater influence upon the rate of change than hydrogen sulphate; so that if we were to add a quantity of a neutral chloride to a solution containing hydrogen sulphate, we should, doubtless, increase the rate of change; for some of the hydrogen sulphate would be replaced by its equivalent (in the ordinary chemical sense) of hydrogen chloride. In the same way it is probable that a solution into which hydrogen sulphate and potassium iodide have been introduced, contains some hydrogen iodide, and that this acid also has its particular effect upon the rate of change, independently of the part which it plays in the reaction itself. If, then, equivalent quantities of hydrogen sulphate and iodide caused equal accelerations, the replacement in the solution of one of these acids by the other would produce no effect; but if hydrogen iodide, like hydrogen chloride, has a greater accelerating power than hydrogen sulphate, the effect of this replacement would be to cause an acceleration independent of, and additional to, that which is due to the increase of iodide. When, as in the preceding sets of experiments, the hydrogen sulphate or chloride replaced by hydrogen iodide is but a small fraction of the whole amount in the solution, this change does not so affect the rates as to hinder us from observing the result of the simple variation of iodide; but when the experiment is pushed further, and a considerable proportion of the acid is thus changed, the effect of this second variation becomes perceptible.

With this limitation, then, that the system must contain free acid enough to render the replacement of a little of it by hydrogen iodide immaterial, the form of the function $\phi(i)$ in the expression $\Sigma = d\,t\,v\,.\,\phi(i)$ has been established by the foregoing experiments, and we may now write the general equation in the form $\Sigma = d\,i\,t\,v\,.\,f(a, b, c, \ldots)$. That is to say, the amount of change varies directly, (1) with the amount of dioxide, and (2) with the amount of iodide in a unit-volume of the solution; (3) with the time during which the change proceeds; (4) with the total volume of the solution; and, finally, with some function of each of the other conditions under which the change occurs.

Of these other conditions, the quantities of hydrogen sulphate,

chloride, and iodide, and the temperature of the solution, have been made the subjects of experiment. Some of the series of experiments are still incomplete, but I may, in conclusion, state summarily the results to which they point.

In a solution containing only hydrogen dioxide and a neutral iodide, the rate of change, though small, is far from being inappreciable. Consequently it cannot be directly proportional to the amount of any acid added to the solution, as we should expect, if with no acid, as with no dioxide or no iodide, there were no change at all. But on comparing the rates at which the change proceeds with successive increments of acid, we find that these rates are in arithmetical progression. If we represent by n the number of I, or millionths of a gramme of combined iodine in one cubic centimetre of a solution, and by α_1, the fraction of dioxide that disappears in a minute, in a solution containing I in one cubic centimetre, at a temperature h; then, as has been shown, in a solution containing n I, the rate of decrease of the dioxide is $n\,\alpha_1$. Again, if there be added to the solution containing I in one cubic centimetre, a unit of some acid, *e. g.*, H_2SO_4, the rate is increased by a certain quantity, and becomes $\alpha_1 + a$, where a is the acceleration due to a unit of hydrogen sulphate, and since the amount of acceleration is found to be proportional to the amount of acid, p units of hydrogen sulphate would produce in this solution a rate $\alpha_1 + p\,a$. Hence, putting α for the rate with n units of iodide and p units of hydrogen sulphate—

$$\alpha = n\,(\alpha_1 + p\,a).$$

The quantity a is a constant, characteristic of the particular acid. Putting a' for the acceleration due to the presence of HCl in a cubic centimetre of the solution, the equation for the rate with any quantities of iodide and hydrogen chloride is similarly

$$\alpha' = n\,(\alpha_1 + p\,a').$$

The effect of neutral salts upon the rate of change appears to be much less than that of acids; but probably each has its effect, and it may be possible to discover new relations between salts and classes of salts by determining their acceleration coefficients.

It is not unlikely that the value of a, for some substances, may be negative; that is to say, that the effect of their introduction into the system may be to cause a retardation proportional to the quantity introduced.

Where two or more substances are introduced at the same time, which do not act chemically one upon another, we may expect each to cause its acceleration independently. In which case, putting p_1, p_2, p_3, . . . for the quantities of the different substances, and a_1, a_2, a_3, . . . for their several coefficients of acceleration, the equation of the rate becomes

$$\alpha = n\,(\alpha_1 + a_1 p_1 + a_2 p_2 + a_3 p_3 + \ldots).$$

Our examination of the effect of varying the one essential condition of the change still remaining, namely, the temperature of the solution, is not yet concluded. But the relation appears to be of this kind. If α be the rate of change in any mixture at 0° C., the rate at any other temperature, say at h degrees, is $\alpha\, k^h$. The value of k is about 1·07; whence it happens, conveniently for the memory, that for every ten degrees C., the rate of change is doubled.

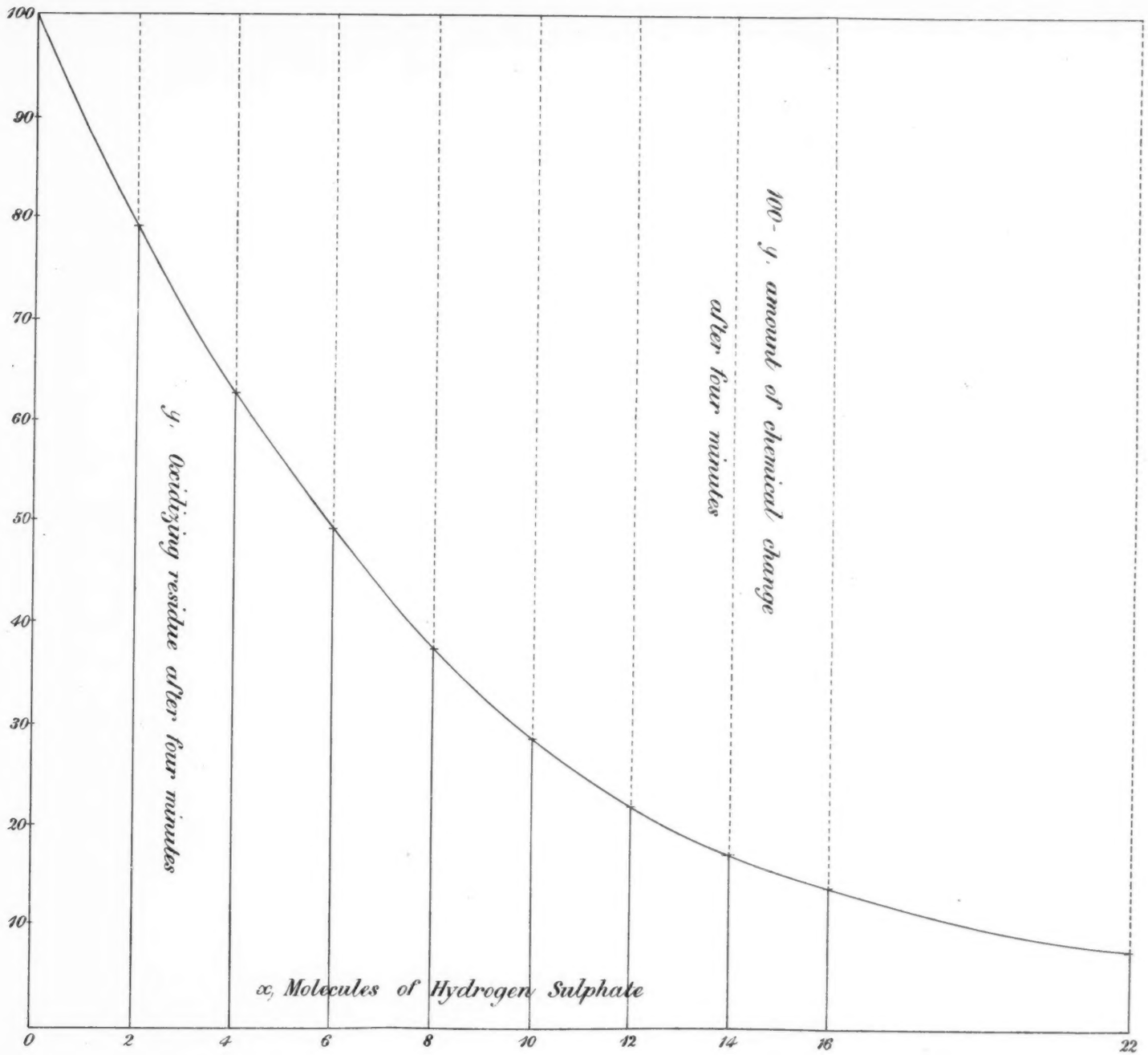
Including this condition, the complete equation of the rate is

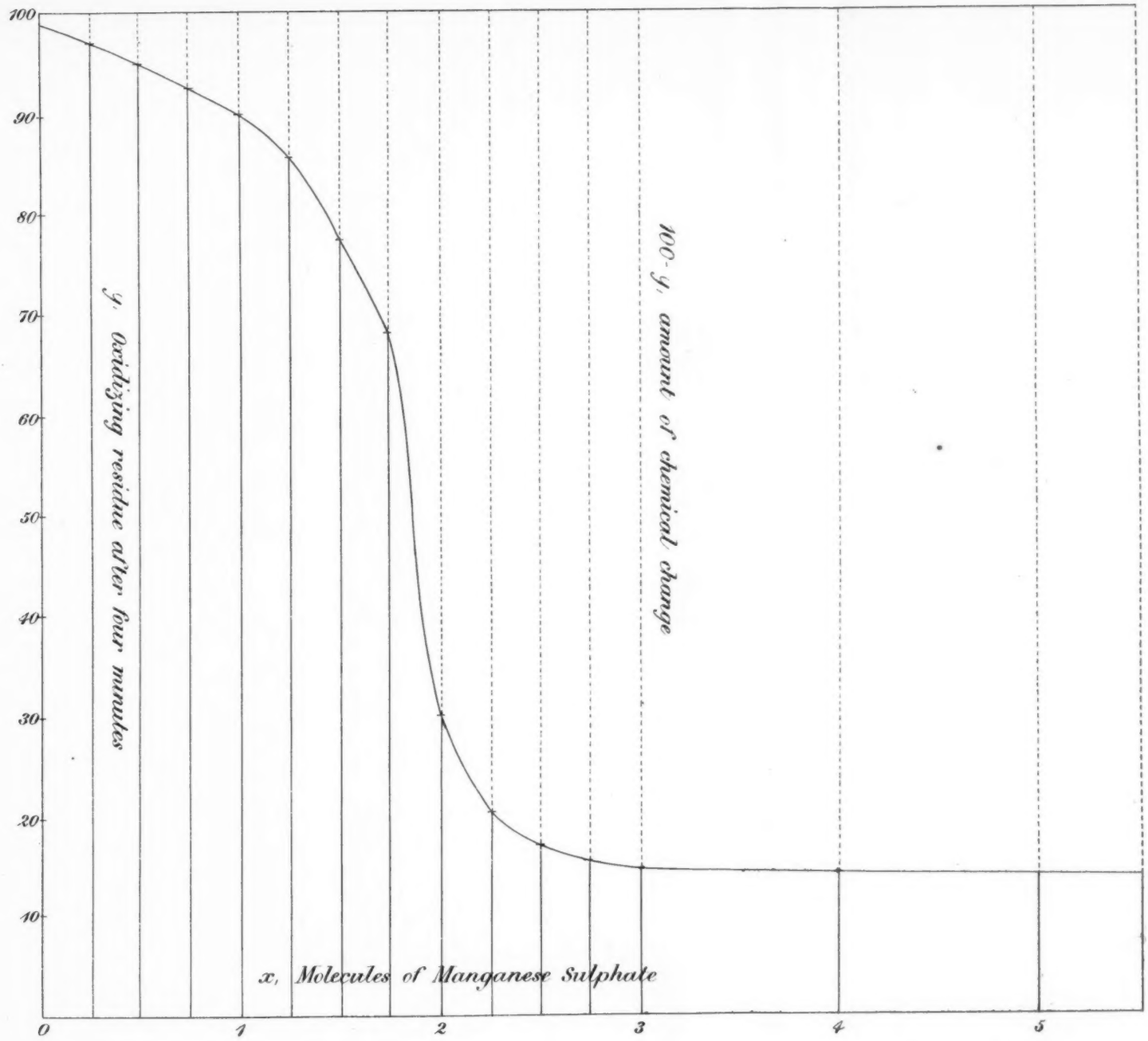
$$\alpha = n\,(\alpha_1 + a_1 p_1 + a_2 p_2 + a_3 p_3 + \ldots)\, k^h,$$

where α_1 is the original rate, a_1, a_2, &c. the several accelerations, at 0° C. Lastly, the total amount of change, under any conditions of the reaction, may be found from the equation

$$\Sigma = d\,i\,t\,v\,(r + a_1 p_1 + a_2 p_2 + \ldots)\, k^h,$$

where r is the fraction of dioxide, which disappears in one minute in a system containing constantly I and H_2O_2 in a cubic centimetre at 0° C.


100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
22
y, Oxidizing residue after four minutes
100- y, amount of chemical change after four minutes
x, Molecules of Hydrogen Sulphate


100
90
80
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1
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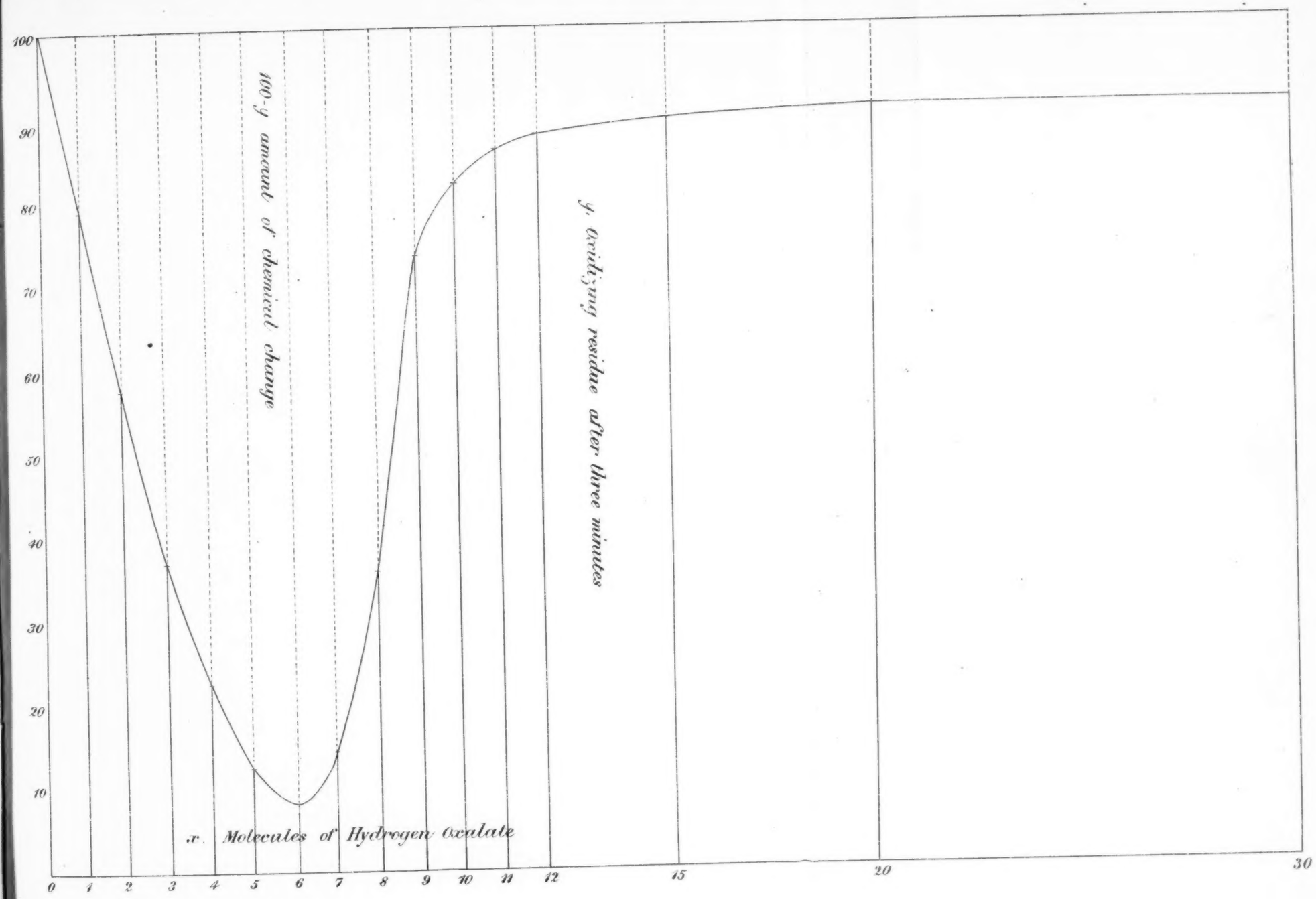
4
5
y, Oxidizing residue after four minutes
100-y, amount of chemical change
x, Molecules of Manganese Sulphate


100
90
80
70
60
50
40
30
20
10
100-y amount of chemical change
y. Oxidizing residue after three minutes
x. Molecules of Hydrogen Oxalate
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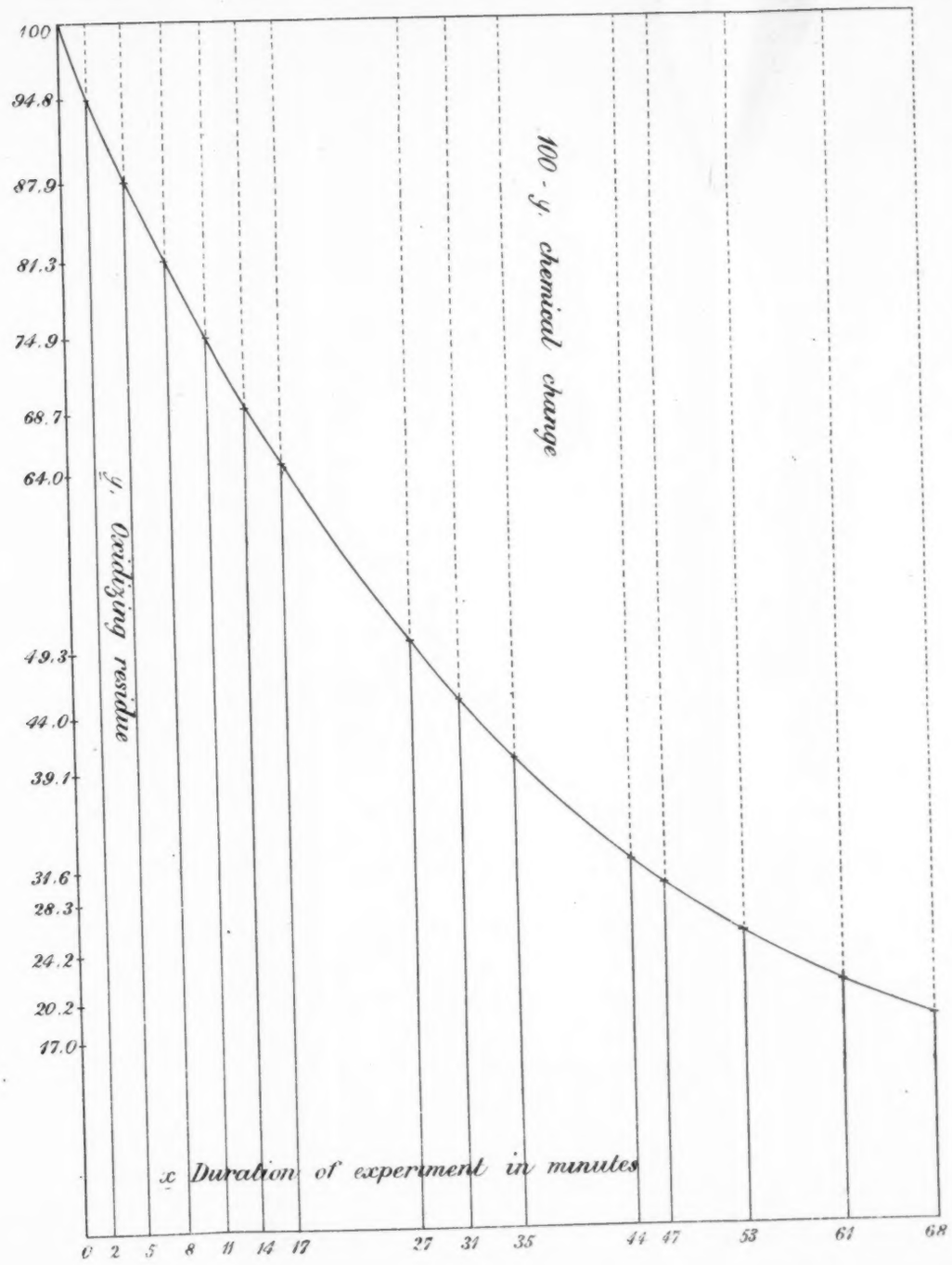
3
4
5
6
7
8
9
10
11
12
15
20
30


100
94.8
87.9
81.3
74.9
68.7
64.0
49.3
44.0
39.1
31.6
28.3
24.2
20.2
17.0
y Oxidizing residue
100 - y chemical change
x Duration of experiment in minutes
0
2
5
8
11
14
17
27
31
35
44
47
53
61
68

XLV.—*On the Estimation of Compound Ethers in Wine.*

By A. Dupré, Ph.D.

Berthelot was, I believe, the first who endeavoured to estimate the amount of compound ethers in wine. He did so by means of a process of titration, also devised by himself. The process consisted, firstly, in estimating the total amount of free acid in the wine by means of a standard solution of baryta; and, secondly, in heating 50 c.c. of the same wine in a closed tube, with a known excess of the same baryta-water, after which the amount of baryta still left unsaturated was determined. During the heating, the compound ethers are decomposed into alcohol and acid, which latter neutralizes part of the baryta. A wine containing any compound ethers will, therefore, neutralize more alkali by being heated with it than it will in the cold; and this excess of alkali neutralized is an exact measure of the amount of acid present as compound ether, and indirectly a measure of its equivalent of alcohol.

With pure compound ethers, or their aqueous or alcoholic solutions, this process gives admirable results, but it is only in exceptional cases applicable to wine, inasmuch as they nearly always contain substances, besides the compound ethers, which neutralize alkalis when heated with them. It is of course totally useless in all cases; where the wine contains an appreciable amount of sugar. The plan proposed in the following pages is free from this objection, whilst it gives, I believe, equally accurate results, even in cases where Berthelot's process is applicable.

The compound ethers present in wine may be divided into two classes, namely: those which are readily volatilized without decomposition, like acetic ether, and those which are not volatile without decomposition, like tartaric ether. If therefore a wine be carefully distilled, part of its ether will pass over into the distillate, part will remain behind in the residue. The ether in the distillate may be estimated by Berthelot's plan, there being nothing present to interfere with it. I am in the habit of using for this purpose a deci-normal solution of soda*, and

* A deci-normal solution of soda contains $\frac{1}{10}$ of an equivalent of caustic soda in 1 litre solution.

heating the ether and alkali in a water-bath, in a long-necked assay flask, closed by a well fitting caoutchouc-stopper, tied down. The heating may be continued from one to five hours without appreciable difference in the result. The ether in the residue is decomposed by heating with the alkali, and the alcohol produced is distilled over and estimated. We thus obtain the amount of acid present in the volatile ethers, and the amount of alcohol present in the fixed ether. By calculation it is of course easy to substitute one for the other in either.

I have satisfied myself by numerous experiments, that if a wine be carefully distilled—from one-half to four-fifths, or even more, being driven over—and the distillate be then again added to the residue in the retort, the amount of free acid present is not appreciably altered by the heating; thereby proving that none of the compound ethers have been decomposed, otherwise the amount of free acid would have increased.

The following examples will show this:—

RHINE WINES.

Rauenthaler, 1862.

50 c.c. wine required 38·0 c.c. deci-normal soda.

300 c.c. of same wine were submitted to distillation, three-fourths driven over; on adding the distillate to the residue 50 c.c. of the mixture required 37·8 c.c. d. n. soda.

Rauenthaler, 1864.

50 c.c. wine required 55·5 c.c. d. n. soda.

50 c.c. wine distilled in water-bath; the distillate added to the residue required 55·3 c.c. d. n. soda.

Hattenheimer, 1862.

50 c.c. wine required 40 c.c. d. n. soda.

50 c.c. wine, distilled over an argand burner, more than one-half driven over; the distillate added to the residue, required 39·9 c.c. d. n. soda.

Sherry, about fifty years in bottle.

50 c.c. wine required 42·7 c.c. d. n. soda.

50 c.c. wine, distilled nearly to dryness in sand-bath, and water added to the residue, which was again distilled nearly to dryness; the distillates added to the residue, required 42 c.c. d. n. soda.

Madeira, bottled in 1817.

50 c.c. wine required 39·7 c.c. d. n. soda.

50 c.c. wine, distilled nearly to dryness in salt-water bath; the distillate and residue required 38·7 c.c. d. n. soda.

It will be seen that, in all cases, the amount of free acid is but slightly altered by distillation, and contrary to what might have been expected, it shows rather a diminution than an increase. Indeed, if the residue in the retort be heated for too long a time, or too strongly, its acidity is almost destroyed, without much more acid passing into the distillate.

As, however, the last traces of free alcohol are not readily distilled off from a wine without danger of decomposing some of its constituents, I prefer to estimate the volatile and fixed ethers in two different quantities :—

1st. From 250 c.c. wine about 200 c.c. are distilled off, and the distillate is made up to 250 c.c. In 100 c.c. of this the free acid is determined by a standard solution of soda, and a second 100 c.c. is heated with a known excess of alkali, as previously described.

2nd. Another 250 c.c. of the wine are evaporated on a water-bath to about 40 c.c. The residue is put into a flask, rendered strongly alkaline by caustic potash or soda, and about three-fourths of it are distilled over. During this distillation the liquid is very apt to froth over, even after addition of tannin, and the distillation must, therefore, be conducted with care. This first distillate, generally strongly alkaline, is rendered slightly acid by sulphuric acid, and again distilled, about 20 c.c. being driven over. These 20 c.c. will contain all the alcohol originally present in the 250 c.c. wine as fixed ether; they contain no appreciable quantity of anything else.

At first I estimated the amount of alcohol in these 20 c.c. by means of their specific gravity, and with the requisite amount of care accurate results may thus be obtained. Inasmuch, however, as the spirit obtained is exceedingly weak, it is very difficult to avoid an error large enough to vitiate the whole result; and, therefore, since the publication of Mr. Chapman's paper on limited oxidation, I estimate the alcohol by converting it into acetic acid, which latter can be accurately and easily determined. The alcohol may also be estimated with tolerable accuracy by means of Geissler's vaporimeter.

For the purpose of oxidation, the 20 c.c. distillate are trans-

ferred to a small strong flask (I make use of the small assay flasks). 10 c.c. of bichromate solution are added, and the flask, after having been securely closed by an india-rubber stopper, tied down firmly, is suspended for one or two hours in a water-bath kept boiling. The bichromate solution contains 10 per cent. bichromate, and enough sulphuric acid to be capable of just forming chrome-alum if all the chromic acid were reduced to chromic oxide, as recommended by Mr. Chapmann. 10 c.c. of such a solution are capable of oxidizing about 0·2 grm. alcohol into acetic acid.

After the flask has been heated for about two hours, it is taken out of the water-bath, cooled, opened, and after the addition of some sulphuric acid, the excess of bichromate left is reduced by zinc. The green solution is next transferred to a small retort, and the acetic acid contained in it is distilled over. This distillation may be conducted either in an oil-bath or over an argand burner, and it is as well to place some pieces of broken tobacco-pipe in the retort to prevent bumping. I have found no difficulty in distilling over all the acetic acid, especially if, after the distillation has been continued nearly to dryness, some more water be added to the residue, and the distillation resumed, repeating the same process two or three times.

The acetic acid in these distillates is then estimated by means of a deci-normal solution of caustic soda, each c.c. of which neutralizes 0·006 grm. $\bar{A}$, and indicates, therefore, 0·0046 grm. alcohol. The total amount of alcohol thus found, divided by 2·5, gives the percentage of alcohol contained in the fixed ethers of the wine.*

* I have used the same method very successfully for estimating the small amount of alcohol excreted through the kidney, after moderately large doses of wine or spirit had been taken. The total amount of urine passed during the 24 hours following the taking of the wine or spirit was collected, and rendered slightly acid; some tannin was added; and the liquid was distilled, about $\frac{1}{3}$ being driven over. This first distillate was then made slightly alkaline, and again submitted to distillation, and this re-distillation repeated, $\frac{1}{3}$ being distilled over each time, until the final distillate amounted to about 20 c.c., in which the alcohol was determined as above. All the distillations of alcoholic liquids, as well as those of acetic acid, were conducted with an apparatus in which the retort, as well as the receiver, was connected, air-tight, with the condenser, the receiver being furnished with a safety-tube closed by mercury. The enclosed air was thus, to a certain extent, allowed to expand or contract, whilst, as long as the distillation is proceeding quietly, the receiver is closed entirely, and all evaporation thus prevented. I was thus enabled to distil either moderately

If a little attention be given to the distillation, it will be found that the distillate containing the acetic acid is quite free from sulphuric acid, and its acidity, as measured by titration, is, therefore, a correct measure of the acetic acid it contains. But even if some sulphuric acid has passed into the distillate, it is nevertheless easy to estimate the acetic acid by titration. We have simply either to divide the distillate accurately into two equal parts, estimating the acidity of one-half directly, whilst the second half is evaporated on a water-bath, and the remaining acidity then determined,—which, being subtracted from the amount found in the first half, leaves the acidity due to the acetic acid;—or, secondly, after having carefully determined the amount of alkali necessary to neutralize the entire distillate, an equal amount of deci-normal sulphuric acid is added, and the whole evaporated to dryness on a water-bath. If the distillate consisted only of acetic acid, the dry residue, on being dissolved in water, will be found to be neutral. Any acidity remaining will be due to sulphuric acid, and has to be subtracted from that first found, to obtain the true measure of the acetic acid.

It will scarcely be necessary to add that if an amount of alcohol be found equal, or approximately equal, to the total amount capable of being oxidized by the bichromate, a second estimation has to be made with more bichromate or less alcoholic solution. I have not, however, as yet, met with any wine which, from 250 c.c., yielded even half the amount of alcohol from its fixed ethers that could be oxidized by 10 c.c. of the above bichromate solution, nor is it at all likely that such a wine exists.

In the following tables, I give the various analytical results upon which the foregoing method is based.

1st. All free alcohol may be expelled by partial evaporation of the liquid on a water-bath.

In half a litre of spirit of 13 per cent. by weight, 20 grm. cane-sugar were dissolved, and the whole was evaporated on a water-bath to 60 c.c. These 60 c.c. were submitted to distillation, 25 c.c. distillate were collected, which, at a temperature of 15·5°, had a spec. gr. of 999·99, water at the same temperature being taken at 1000.

strong or very diluted spirits, even four or five times, without any appreciable loss of alcohol.

2nd. No acid tartaric ether is decomposed or volatilized during such evaporation.

A dilute solution of acid tartaric ether in spirit of 10 per cent. was prepared, containing in 20 c.c. an amount of acid, neutralized in the ether, equivalent to 10·1 c.c. d. n. soda. The free acid present in 20 c.c. of the mixture required 28·2 c.c. d. n. soda. Four quantities of 20 c.c. each were next put into small porcelain dishes, and heated on a water-bath; the first was allowed to evaporate to $\frac{1}{4}$, the second to $\frac{1}{10}$, the third just to dryness, and the fourth was heated on the water-bath for an hour after it had become dry; the free acid in all the samples was then again determined.

20 c.c. of the original mixture required			28·2	c.c. d. n. soda	
The residue from the	first dish	„	28·2	„	„
„ „	second	„	28·4	„	„
„ „	third	„	28·4	„	„
„ „	fourth	„	28·0	„	„

thus showing an exceedingly slight alteration only had taken place.

3rd. Two solutions of pure tartaric ether in alcohol being made, the amount of alcohol present as ether in each was estimated by titration; to the weaker of the two, 4 per cent. cane-sugar were next added, and the alcohol present in the ether was then also estimated by the process given above. For this purpose, $\frac{1}{2}$ litre of each solution was evaporated on a water-bath to 60 c.c.; this residue was rendered strongly alkaline and distilled; and the first distillate after being acidified was re-distilled, 28·5 c.c. of the second distillate being collected in each case. These second distillates had, at a temperature of 15·5°, a sp. gr. of 997·50 and 998·30, showing a strength of 1·34 per cent. and 0·91 per cent. by weight respectively, which, calculated upon the $\frac{1}{2}$ litre taken, gives 0·0760 and 0·0520 per cent. alcohol present as ether in the two mixtures. Titration had given 0·08004 and 0·05428 per cent. We have therefore—

	By titration.	By evaporation, &c.
In 1st mixture.....	0·08004	0·0760
„ 2nd „	0·05428	0·0520

Lastly, two very dilute spirits were prepared, by carefully mixing the requisite weights of absolute alcohol and water, containing in 20 c.c. 0·1 grm. and 0·025 grm. of absolute alcohol.

In 20 c.c. of these mixtures the alcohol was oxidized by bichromate solution, in the manner before described, and the resulting acetic acid estimated by titration. The distillate from the stronger mixture required 20·1 c.c. d. n. soda solution for neutralization, equivalent to 0·0924 grm. alcohol; the distillate from the weaker mixture required 5·5 c.c. d. n. soda, equivalent to 0·0253 grm. alcohol.

1st. Alcohol taken 0·1 grm. found 0·0924 grm.
2nd. „ 0·025 „ „ 0·0253 „

Application of the Method to Wine.

In the case of light wines, containing but little or no sugar and extractive, it is sufficient, in estimating the alcohol of their fixed ether, simply to evaporate them to about $\frac{1}{5}$th or $\frac{1}{10}$th their bulk; with strong wines containing much sugar it is, however, advisable, either to dilute them considerably before evaporation, or, after they have been evaporated to $\frac{1}{5}$, to dilute the residue with 100 c.c. or 200 c.c. water, and once more evaporate down to about 40 c.c. In either case the residue is distilled with alkali, &c., &c., as previously described. The alcohol in the second distillate may be estimated by its specific gravity, using Geissler's vaporimeter, or, most accurately, by oxidation and estimation of the acetic acid formed. If care be taken, all three methods give the same result.

Berthelot has given a formula by means of which the total amount of alcohol contained as ether in any wine, when etherification is complete, can be calculated from the known amount of free acid and alcohol present. For the sake of comparison I have added this theoretical number to each analysis; in young wines the amount of ether found should fall below this theoretical value, whilst in older wines the two values should agree.

RHINE WINES.

Rauenthaler, 1864.—18*s*. per dozen.

Alcohol	7·44 per cent., by wt.
Total free fixed acid calculated as $\bar{T}$	0·674 per cent.
„ volatile „ „ $\bar{A}$	0·118 per cent.
Total dry residue	2·207 per cent.
Sugar	traces.

Estimation of Alcohol in fixed Ethers.

a. Alcohol estimated by specific gravity.

1 litre of wine was distilled in a salt water-bath; 900 c.c. distilled over; the residue was rendered strongly alkaline, and the distillation proceeded with; 60 c.c. were collected, which, at a temperature of 15·5° C., had a sp. gr. of 999·14, showing 0·45 per cent. by weight of alcohol, or 0·027 per cent. of original wine.

300 c.c. wine distilled over an argand lamp; 200 c.c. passed over, residue treated as above, but the first distillate was rendered acid and again distilled; 25 c.c. off second distillate collected, which had, at a temperature of 15·5° C., a sp. gr. of 999·45, showing 0·29 per cent. alcohol, or 0·024 per cent. of original wine.

b. Alcohol estimated by oxidation.

250 c.c. wine evaporated on a water-bath to 50 c.c.; residue rendered alkaline and distilled; first distillate acidified and redistilled; second distillate of 20 c.c. oxidized by bichromate solution as before described. Acetic acid obtained on distillation, neutralized 14·2 c.c. d. n. soda, equivalent to 0·0653 grm. alcohol, or 0·0261 per cent. of wine.

100 c.c. wine, evaporated on water-bath to 25 c.c., residue treated as above. Ā obtained neutralized 6·0 c.c. d. n. soda, equivalent to 0·0276 per cent. alcohol in wine.

250 c.c. wine, evaporated to 25 c.c. Ā obtained neutralized 12·6 c.c. d. n. soda, equivalent to 0·05796 grm. alcohol, or 0·0232 per cent. of wine.

We have therefore alcohol present in fixed ethers—

1st	0·0270	per cent.
2nd.....	0·0240	„
3rd	0·0261	„
4th	0·0276	„
5th	0·0232	„
Mean....	0·0256	„ of wine.

Alcohol in volatile ethers, found by titration.....	0·0175	per cent.
Total alcohol in ethers found.....	0·0431	„
Total alcohol in ethers calculated ..	0·0581	„

Rauenthaler, 1862.—54*s*. per dozen.

Alcohol	8·83	per cent. by weight.
Free fixed acid, as $\bar{T}$	0·445	„
Free volatile acid as $\bar{A}$	0·178	„
Total dry residue	1·867	„
Sugar	0·062	„

Fixed Ethers.

a. Alcohol estimated by vaporimeter.

Half a litre of wine evaporated on water-bath to 125° c.c.; residue treated as above; second distillate amounted to 25 c.c., showing by vaporimeter 0·45 per cent. alcohol by weight, equal to 0·0225 per cent. of wine.

b. Alcohol estimated by oxidation.

300 c.c. wine evaporated to 20 c.c.; residue treated as above. $\bar{A}$ obtained neutralized 14·5 c.c. d. n. soda, equivalent to 0·0667 grm. alcohol, or 0·0222 per cent. of wine.

250 c.c. wine evaporated to 50 c.c.; residue treated as above. $\bar{A}$ obtained neutralized 11·3 c.c. d. n. soda, equivalent to 0·05198 grm. alcohol, or 0·0208 per cent. of wine.

1st	0·0225	per cent.
2nd.....	0·0222	„
3rd	0·0208	„
Mean....	0·0218	„

Alcohol in volatile ethers by titration..	0·02392	per cent.
Total alcohol in ethers found	0·04572	„
Total alcohol in ethers calculated	0·045957	„

Hattenheimer, 1862.—40*s*. per dozen.

Alcohol	9·97	per cent. by weight.
Free fixed acid as $\bar{T}$	0·525	„
Free volatile acid as $\bar{A}$	0·067	„
Total dry residue	2·235	„
Sugar	0·017	„

Fixed Ethers.

a. Alcohol estimated by specific gravity.

300 c.c. wine distilled; two-thirds distilled over; residue treated

as above; second distillate amounted to 25 c.c., having a specific gravity of 999·58, showing 0·22 per cent. alcohol, or 0·0183 per cent. of wine.

b. Alcohol estimated by vaporimeter.

The above 25 c.c. gave by vaporimeter 0·25 per cent., or 0·0208 per cent of wine.

c. Alcohol estimated by oxidation.

250 c.c. wine evaporated to 40 c.c. $\bar{A}$ obtained neutralized 11·4 c.c d. n. soda, equivalent to 0·05244 grm. alcohol, or 0·0209 per cent of wine.

250 c.c. wine evaporated to 30 c.c. $\bar{A}$ obtained neutralized, 11·2 c.c. d. n soda, equivalent to 0·05152 grm. alcohol, or 0·0206 per cent of wine.

1st	0·0183	per cent.
2nd.....	0·0208	„
3rd	0·0209	„
4th	0·0206	„
Mean....	0·0201	„

Alcohol in volatile ethers by titration ..	0·0253	per cent.
Total alcohol in ethers found.....	0·0454	„
Total alcohol in ethers calculated	0·0521	„

Steinberg Cabinet, 1858.—120*s.* per dozen.

Alcohol.....	9·74	per cent.
Free fixed acid as $\bar{T}$	0·4113	„
Free volatile acid as $\bar{A}$	0·1305	„
Total dry residue	2·073	„
Sugar	none.	

Fixed Ethers.

300 c.c. wine evaporated to 20 c.c.; residue treated as usual. $\bar{A}$ obtained neutralized 14·5 c.c. d. n. soda, equivalent to 0·0667 grm. alcohol, or 0·0222 per cent. of wine.

250 c.c. wine evaporated to 50 c.c. $\bar{A}$ obtained neutralized 13·4 c.c. d. n. soda, equivalent to 0·06164 grm. alcohol, or 0·0246 per cent. of wine.

1st	0·0222 per cent.
2nd	0·0246 „
Mean....	0·0234 „

Alcohol in volatile ethers by titration..	0·02944 per cent.
Total alcohol in ethers found	0·0528 „
Total alcohol in ethers calculated	0·0499 „

Light Claret, 1865.—15*s.* per dozen.

Alcohol.....	9·05 per cent.
Free fixed acid as $\bar{T}$	0·338 „
Free volatile acid as $\bar{A}$	0·222 „
Total dry residue	2·167 „
Sugar	0·047 „

Fixed Ethers.

250 c.c. wine evaporated to 15 c.c. $\bar{A}$ obtained neutralized 7·4 c.c. d. n. soda, equivalent to 0·03404 grm. alcohol, or 0·0136 per cent. of wine.

250 c.c. wine evaporated to 40 c.c. $\bar{A}$ obtained neutralized, 8·3 c.c. d. n. soda, equivalent to 0·03818 grm. alcohol, or 0·0152 per cent.

1st	0·0136 per cent.
2nd.....	0·0152 „
Mean....	0·0144 „

Alcohol in volatile ethers	0·0170 per cent.
Total alcohol in ethers found.....	0·03140 „
Total alcohol in ethers calculated..	0·05056 „

Cape Wine.—18*s.* per dozen.

Alcohol.....	24·1 per cent. by wt.
Free fixed acid as $\bar{T}$	0·2244 „
Free volatile acid as $\bar{A}$	0·1470 „
Total dry residue.....	6·18 „
Sugar.....	2·88 „

250 c.c. wine, evaporated to 40 c.c. $\bar{A}$ obtained neutralized

15·9 c.c. d. n. soda, equivalent to 0·07314 grm. alcohol, or 0·0292 per cent. of wine.

250 c.c. wine, evaporated to 25 c.c. Ā obtained neutralized 15·9 c.c. d. n. soda, equivalent to 0·07314 grm. alcohol, or 0·0292 per cent. of wine.

1st	0·0292	per cent.
2nd	0·0292	„
Mean....	0·0292	„

Alcohol in volatile ethers	0·03348	per cent.
Total alcohol in ethers found	0·0627	„
Total alcohol in ethers calculated..	0·08276	„

Port.—1864.

Alcohol	18·56	per cent.
Free fixed acid as T̄	0·3075	„
Free volatile acid as Ā	0·0840	„
Total dry residue	7·305	„
Sugar	4·905	„

Fixed Ethers.

250 c.c. wine, evaporated to 40 c.c.; 200 c.c. water added, and again evaporated to 40 c.c.; residue then treated as before described. Ā obtained neutralized 16·4 c.c. d. n. soda, equivalent to 0·07544 grm. alcohol, or 0·030176 per cent. of the wine.

Alcohol in volatile ethers	0·01288	per cent.
Total alcohol in ethers found	0·043056	„
Total alcohol in ethers calculated..	0·062023	„

I am now engaged in the examination of a great variety of wines, and hope in a future communication to be able to show the influence which age, climate, addition of alcohol, etc., etc., have on the quantity and quality of the compound ethers of the wine.

Laboratory, Westminster Hospital,
September 10, 1867.

XLVI.—*Researches on Gun-cotton.—Second Memoir. On the Stability of Gun-cotton.*

By F. A. Abel, F.R.S., V.P.C.S.*

The earlier of the published researches into the composition and properties of gun-cotton were speedily followed by accounts of the spontaneous decomposition which the substance was, in many instances, observed to undergo upon more or less protracted exposure in confined spaces to strong or diffused light. These indications of instability, in conjunction with the occurrence of several serious explosions during the manufacture of gun-cotton in France and England, afforded apparently good grounds for the general conclusion,—arrived at within a brief period after the announcement of Schönbein's discovery, and adhered to until quite recently in all countries except Austria,—that this remarkable explosive agent did not in itself possess the quality of uniform permanence essential to its safe manufacture, or to its employment with any degree of security from accident, in warlike or industrial operations.

It is unnecessary to refer in detail to the results of the numerous observations published before 1860 upon the spontaneous changes which particular specimens of gun-cotton had suffered. In the brief prefatory review of published investigations upon the production and composition of gun-cotton, contained in the paper on those subjects which I communicated to the Royal Society last year, it has been shown that the products obtained by individual operators in submitting cotton to the action of nitric acid varied greatly in composition, and that, with only one or two exceptions, these could not be viewed as representing the definite substance producible by the most complete action at a low temperature of a mixture of the strongest nitric and sulphuric acids upon purified cotton-wool (or nearly pure cellulose). The behaviour and results of the decomposition of such specimens, or of others of more recent date prepared (for lectures or similar experimental purposes) without special regard being paid to their composition or purity, afford but little information that can be accepted as

* Abridged from Phil. Trans., part I, 1867.

bearing upon the question of stability of gun-cotton when produced by a system of operation which is now known to furnish uniform products in a condition of comparative purity.

There can be no question that the variations in composition of the different specimens of gun-cotton, the decomposition of which has received investigation at different hands, exerted a most important influence upon the period for which they withstood the destructive effects of heat and light, and upon the *degree of rapidity* with which chemical change, when once established, proceeded from stage to stage. The *products* of change described by different observers have also varied somewhat in their characters, partly on account of the variations in the gun-cotton itself, and partly because different experimenters have examined the products of its metamorphosis at different stages.

The accounts published by De Luca, Bonet, and Blondeau, between 1861 and 1865, of their investigations into the changes which gun-cotton undergoes spontaneously, include nearly all the results previously described in one or other of the published papers on this subject.

The following is a general statement of the changes which gun-cotton, preserved in bottles partly or perfectly closed, has been observed to undergo by exposure to light, and of the nature of the products of decomposition.

In the first instance nitrous vapours make their appearance, the atmosphere in the vessel becoming sometimes of a deep orange tint. The gun-cotton acquires considerable acidity, exhibits a peculiar pungent odour, and gradually contracts, so that it eventually occupies only a small proportion of the original volume. During this period a considerable proportion of nitric acid accumulates in the mass, and the decomposition proceeds after a time with increased rapidity, especially if the vessel be exposed to sunlight. The contracted gun-cotton gradually becomes more or less friable; its explosiveness is notably reduced; and it yields a highly acid extract to water, in which, besides nitric acid, small proportions of glucose, of formic and oxalic acids, and of cyanogen have been detected. The material sometimes contracts to such an extent as to form a very compact somewhat hard mass, but in general it ultimately passes over with more or less rapidity into a brownish gum-like mass, which at first is rendered very porous by

the evolution of gas-bubbles, and becomes lighter in colour and friable after a time. This ultimate product of the decomposition of gun-cotton has been found to contain glucose and oxalic acid in considerable proportions, besides a gum-like substance, formic acid, cyanogen, and an organic acid, which, by some observers, is considered to possess novel characters, and Divers believes that he has identified pectic and parapectic acids in the product of a decomposed specimen.* The amorphous mass has also been found to evolve ammonia when heated with a solution of potassic hydrate.

In some instances the gun-cotton is described as having undergone other intermediate changes, but the greatest discrepancies exist between the observations of even the most practised experimenters regarding the periods within which the decomposition of gun-cotton has become manifest, and the conditions under which the changes have occurred. In some instances the first signs of decomposition were observed after exposure of the gun-cotton to daylight for several years, in others a few days' exposure sufficed to establish the change. Some observers state that the material has been preserved in the dark for very protracted periods without change, others (*e.g.* quite recently De Luca and Blondeau) show that, even in the dark, gun-cotton undergoes decomposition within a comparatively short period. Such conflicting observations afford convincing proof of great variations in the composition or degree of purity of the materials experimented upon.

The exposure of gun-cotton to heat has, by most observers, been found to accelerate its decomposition considerably; but here again great discrepancies are presented by different

* The observations of Divers regarding the occurrence of the pectic acids among the products of decomposition of gun-cotton, have been confirmed by the results of examination of a very large number of specimens obtained by the decomposition of gun-cotton at high temperatures under various conditions. The reactions of pectic and of para- and meta-pectic acids have been so frequently obtained that these substances must be regarded as general products of the gradual decomposition of gun-cotton. On the other hand, although the most careful search has frequently been made for glucose, only two instances of its existence were established by the fermentation test. It appears probable that the reduction of cupric salt from an alkaline solution has in many instances been accepted as a sufficient indication of the presence of glucose, while, in reality, this reaction has been furnished by the pectic acids produced. Small quantities of cyanogen have on several occasions been detected among the products of very gradual decomposition of gun-cotton by heat.

accounts of the behaviour of the material under the influence of different temperatures; thus, its spontaneous explosion has been brought about in some instances by brief exposure to a degree of heat which, in others, has only produced a comparatively very gradual decomposition.

The most interesting and important of recent observations upon the influence of heat on the stability of gun-cotton are those described by Pélouze and Maurey in their recent report upon Baron Von Lenk's system of manufacturing gun-cotton, and upon the composition and properties of the products which it furnishes. They describe a number of results obtained with specimens of gun-cotton which, it is to be inferred, were all produced according to Von Lenk's directions, and which, therefore, provided these were strictly adhered to, and such an adherence ensured the uniformity of the products, should have furnished reliable data regarding the powers of purified gun-cotton to resist the destructive effects of heat. The principal results arrived at by Pélouze and Maurey are as follows: they found that all specimens which were heated to 100° C. became decomposed in more or less time; a few minutes' exposure to that temperature sufficed in every instance to determine the evolution of nitrous vapours. They describe the results of decomposition as susceptible of variation at will; either the gun-cotton might be brought to explode, or the various forms of decomposition already described by other chemists might be established; or finally, it might be made to furnish simply a small black residue presenting the appearance of carbon, from which ammonia might be disengaged. Identically the same results were obtained by exposing specimens of gun-cotton to temperatures of 90° and 80° C., with this difference, that the phenomena of decomposition, instead of appearing in a few minutes, were not exhibited until after the lapse of several hours. It is further stated that pyroxylin is decomposed at 60° C. (140° F.), and even at 50° C. (122° F.); after the lapse of several days dense vapours filled the vessel containing the specimens, but no explosions of gun-cotton occurred in the experiments conducted at those temperatures. Great stress is laid, however, upon an instance of explosion which occurred with a specimen of gun-cotton prepared according to Von Lenk's process, immediately upon its coming into contact

with the metal of an oil-bath, the temperature of which was only 47° C. (116°·6 F.) at the time. Pélouze and Maurey afterwards refer to the instances of spontaneous decomposition of gun-cotton at ordinary temperatures observed by other chemists, and to certain specimens, among a number prepared at Bouchet in 1847, which had undergone alterations such as have already been described. These were examined for sulphuric acid, and none was detected; hence the conclusion is drawn that these samples had been perfectly washed, and that their spontaneous change could not be ascribed to imperfect purification. It is argued that instances of change have been observed to occur under ordinary atmospheric conditions, similar to those established in gun-cotton at higher temperatures; that, because exposure to the latter had occasionally brought about spontaneous explosion, it is possible for instances of spontaneous decomposition at *ordinary* temperatures to result in explosions, and that, consequently, it is right to conclude that the storage of large quantities of gun-cotton is attended with great risk of explosion. In further support of this conclusion the observations are recorded, that the most perfectly washed gun-cotton becomes acid by long exposure to sunlight; that some pyroxylin, which was alkaline at first, after exposure for several weeks to light, in contact with the sides of a glass flask, exhibited an acid reaction; and that, even when gun-cotton is preserved in the dark, this acidity invariably becomes manifest in course of time. Finally, without referring to any single instance in which an explosion or even an appreciable development of heat has been observed as resulting from protracted exposure of gun-cotton to strong daylight or sunlight, Pélouze and Maurey conclude that the indications of gradual decomposition furnished by certain specimens of gun-cotton under those conditions, are sufficient proof of the liability of this material, as now manufactured, to explode spontaneously, when stored in considerable quantities.

The researches into the manufacture, composition, and properties of gun-cotton, upon which, as a member of the Government Gun-cotton Committee, I have been engaged for nearly four years, have included, from their very commencement, careful observations, and a great variety of experiments, with both small and large quantities of material, bearing upon the influence

exerted by light and heat, and by various modifications introduced into the system of manufacture, upon the stability of gun-cotton produced in accordance with the general directions laid down by Von Lenk. It is obvious that, although most of these experiments have furnished very decisive results within a comparatively brief period, there are others which become the more valuable and the more fully conclusive in their character, the longer the period of their duration. It is considered, however, that the data which even the latter class of experiments has already furnished, possess sufficient scientific interest and practical importance to warrant their present publication, in addition to those obtained by numerous experiments instituted with the view to ascertain whether and to what extent the results of researches recently published in France upon the spontaneous changes of gun-cotton, apply to the material manufactured in this country during the last four years.

The experiments and observations carried on at Woolwich may be classed as having for their objects,—

(*a.*) The determination of the influence of light and of long protracted storage, under ordinary conditions as to temperature, upon the stability of gun-cotton;

(*b.*) The investigation of the behaviour of gun-cotton upon exposure, under varied conditions, to artificial temperatures and to such elevated natural temperatures as are occasionally experienced in particular localities;

(*c.*) The examination of the influence exerted upon the stability of gun-cotton by special modes of preparing and preserving it.

A few observations have been made upon specimens of gun-cotton which either were prepared by myself or came into my possession previous to the commencement of the present inquiry, but all actual experiments have been instituted with samples of products of manufacture obtained at Hirtenberg, Stowmarket, and Waltham Abbey, some modifications having been introduced, in special instances, in the ordinary system of operation at the last-named manufactory, with the view to ascertain the nature and extent of their influence upon the stability of the product.

Part I.—Action of Light upon Gun-Cotton.

The want of uniformity in power to resist the destructive action of light, exhibited by different specimens of gun-cotton with which chemists have experimented, has been additionally exemplified by the behaviour of numerous specimens of gun-cotton which have from time to time come into my hands or were prepared by me, previous to 1862. I will limit my notice of such specimens to two examples.

In the autumn of 1846 one or two pounds of gun-cotton were prepared by me at the Royal College of Chemistry, according to the directions which had been made public in Germany a short time previously. The product, which was insoluble in mixtures of ether and alcohol, was obtained by immersing carded and purified cotton-wool of very high quality for a few minutes in the prescribed mixture of nitric and sulphuric acids, afterwards exposing it for several hours to a current of water, then digesting it in a cold dilute solution of potassic carbonate, and finally washing it in pure water. The larger proportion of the product was gradually expended in lecture-experiments, but a specimen has been preserved by me up to the present time. For sixteen years it was simply enveloped in paper and kept in a drawer much used; at the expiration of that period, when it was found to be perfectly unchanged, not exhibiting the slightest acidity or odour, it was transferred to a stoppered bottle, in which it has been since exposed to diffused daylight for four years. This specimen still remains perfectly unchanged.

Messrs. Hall, of Faversham, had the goodness, about three and a half years ago, to disinter at my request a sample of a large quantity of gun-cotton manufactured by them in 1847, and which they buried upon the occurrence of the disastrous explosion at their works in that year. This sample was much discoloured when received, but the fibre was strong, and the material did not appear to have undergone any change. Its explosive properties were, however, considerably inferior to those of gun-cotton prepared according to Schönbein's or Von Lenk's directions; and, upon analysis, it furnished results corresponding very nearly with those required by the formulæ $C_{18}H_{23}O_{15}7NO_2$, the compound C, or collodion gun-cotton, of which the composition was determined by Hadow. It was,

moreover, readily soluble in a mixture of ether and alcohol, and furnished a good collodion-film. It is most probable, therefore, that a deficiency in the strength of the acids employed in its production had led to the manufacture, in this instance, of soluble and less explosive gun-cotton by Messrs. Hall. A specimen of this material, after having been very carefully washed, was dried and enclosed by me in a stoppered bottle, in which it has remained exposed to diffused daylight for upwards of three years. A piece of litmus-paper, enclosed with the gun-cotton, exhibited faint signs of reddening within three months after the first exposure, and within twelve months it was bleached. At this time the gun-cotton possessed a faint but decided cyanic odour; no nitrous vapours were perceptible within the bottle, either then or at any more recent period up to the present time, though the odour of the gun-cotton has now become more pronounced, and is indicative of nitrous acid. The substance has at present a marked acid reaction; it has not as yet altered either in explosiveness, strength of fibre, and other properties, but the odour and slight development of acid are undoubted indications that the material which for sixteen years was preserved in a moist condition in the dark, without any apparent change, has during three years' exposure to light furnished slight indications of spontaneous change. It was a specimen of gun-cotton prepared by Messrs. Hall, in 1847, and preserved by Percy since that year in a stoppered bottle, exposed to light, which had gradually become converted into a light-brown semifluid gum-like mass, described by Hofmann as having exhibited all the properties of ordinary gum, and as being interspersed with crystals of oxalic acid. It is therefore not improbable that the specimen of Messrs. Hall's manufacture above referred to may, by long-continued exposure to light, eventually furnish more important indications of spontaneous change than have hitherto been developed in it.

There can be little doubt that the quality of cotton operated upon by Messrs. Hall in the production of the specimens above referred to (and certainly in the instance of that examined by me), was considerably inferior to that of the material employed by me in 1846, and the character of the gun-cotton produced demonstrates that the conditions essential to the production of the most explosive material were not fulfilled by the method of manufacture pursued by those gentlemen in 1847. It is equally

certain that the great importance of as complete a purification as possible of the cotton employed and of the product obtained was not fully recognized at that period, and that consequently, although a small laboratory operation carefully conducted according to the prescribed directions might furnish a pure product of great stability, the operations of manufacture had not been established with the precision essential to the attainment of satisfactory results.

The following are the results obtained up to the present time by exposure to light, under various circumstances, of gun-cotton prepared and purified according to Von Lenk's directions.

Exposure to strong daylight and to sunlight, either in the open air or in confined spaces for a few days (two to four), developes in the gun-cotton a very faint aromatic odour; and if litmus-paper be allowed to remain in close contact with the confined material, it acquires a rose-coloured tinge similar to that produced by carbonic acid, and recovers its original colour after brief exposure to air. If, after exposure to light in open air for some days, the gun-cotton be placed in the dark, in cases which are not air-tight, the odour becomes gradually fainter, and the effect upon litmus-paper slighter; if the packages containing the gun-cotton are air-tight, the odour and action upon litmus do not increase during storage for several years (the actual experience gained at Woolwich extends over four years).

If the gun-cotton be exposed for protracted periods to daylight with free access of air, it speedily loses all odour and power of affecting litmus. If exposure to diffused daylight in confined spaces be continued, the first results of the action of light are, of course, retained; but up to the present time no single indication of their increase has been observed; indeed, the very faint acid reaction described, which was developed at first, has frequently disappeared, probably in consequence of the neutralizing action of small quantities of earthy carbonates contained in the gun-cotton.

But if the material be exposed continuously in a perfectly confined space to the action of sunlight or strong daylight, it furnishes, after a time, much greater evidence of change than that already described. The acidity gradually becomes more manifest; the odour increases, and becomes in time somewhat pungent and indicative of the presence of very small quantities

of nitrous acid; and litmus-paper, if confined in the vessel with gun-cotton thus exposed, becomes entirely bleached after two or three months. Although specimens of gun-cotton always undergo some spontaneous change under these very special circumstances, the decomposition proceeds with extreme slowness; and the results of the observations instituted by me are, therefore, in this respect, quite at variance with those recently published by De Luca, who states that the specimens operated upon by him decomposed upon exposure to sunlight, some on the first day of the experiment, others after several days' exposure.

The following account of special experiments instituted with gun-cotton manufactured at Waltham Abbey, will serve to illustrate the rate and nature of the decomposition suffered by this material when exposed to the action of sunlight in confined spaces.

Experiments 1 and 2.—16·37 grms. of air-dry gun-cotton were introduced into a large bulb blown at the extremity of a barometer tube of 10 millims. internal diameter, the length of which below the bulb was 812 millims. The bulb-tube was supported with the open extremity dipping into mercury.

19·12 grms. of the same gun-cotton were placed in a bulb-tube with a stem of the same length. The extremity of this tube was also dipped into mercury; but a small quantity of water was afterwards passed up into the end of the tube, so that the gun-cotton in the bulb might receive the maximum proportion of moisture which it was capable of absorbing. On the 20th of October, 1863, these two samples of gun-cotton were placed in a very exposed position out of doors in front of a brick wall, where sunlight had access to them during the greater part of the day; moreover, during the summer months, the heat radiated from the wall immediately behind the bulbs was considerable. The appearance of the gun-cotton and of the atmosphere in the bulbs was carefully examined periodically, but the former retained its original appearance, and no coloration by nitrous acid was ever observed in the latter. On the 1st of December, 1864 (more than thirteen months after the commencement of the experiments), the tube enclosing the gun-cotton in a moist atmosphere was accidentally broken. The contents of this bulb were therefore removed and examined. The gun-cotton was found to have a powerful acid reaction and a

somewhat pungent odour, its fibre had become tender, but its explosiveness had not sustained any important diminution. The aqueous solution yielded upon evaporation only a very small amorphous residue, which consisted partly of alkaline and earthy salts derived from the gun-cotton. By exhausting one gramme of the material with water, neutralizing the solution with sodic carbonate and concentrating by evaporation, abundant evidence of the presence of nitric acid was obtained. The aqueous extract acquired a yellowish colour upon addition of potassic hydrate, and a small quantity of cupric salt added to the alkaline liquid was reduced when heat was applied.

After treatment with water, the gun-cotton furnished about 18 per cent. of matter soluble in a mixture of ether and alcohol. The solution, upon evaporation, furnished a horny brittle residue, which was explosive, and appeared to possess the characters of the lower nitrocellulose, $C_{18}\left\{\begin{matrix}H_{22}\\8N\Theta_2\end{matrix}\right\}\Theta_{15}$. The acidity of the gun-cotton was determined in 5 grms. of the specimen, and was found to correspond to 2 per cent. of $HN\Theta_3$.

A portion of this altered gun-cotton was placed in a stoppered bottle immediately upon removal from the bulb, and set aside in a cupboard to which light had imperfect access. After the lapse of two years (upwards of three from the commencement of the experiment) the specimen was again examined. Upon opening the bottle a faint odour of nitrous acid was perceived. A number of small very hard crystals were found firmly attached to the glass; and similar crystals were interspersed through the material itself, which still retained the appearance of the original gun-cotton, having, however, contracted to some extent. On removal from the bottle it was found to be quite pulverulent; it speedily attracted moisture from the air, passing over into a very adhesive mass; it was soluble in water; the solution, which was turbid only from suspended mineral matter, reduced cupric salts abundantly, and gave the reactions of parapectic acid, but was not found to contain glucose.

A portion of the specimen of air-dry gun-cotton which had been enclosed with ordinarily dry air in a bulb-tube at the same time as the sample just referred to, was also examined after it had been exposed for thirteen months, the remainder being left in the bulb, and its exposure continued for a further period of two years. The effects upon this specimen of more than one

year's exposure in a confined space to strong daylight, frequent sunlight, and considerable heat radiated from the wall during the summer months, were as follows:—The gun-cotton had a somewhat pungent odour, in which, however, nitrous acid could not be recognized; its reaction was decidedly, though not powerfully, acid; the strength of its fibre and its explosiveness had not become affected. By exhaustion with boiling water it furnished a somewhat acid liquid, which contained a very small quantity of organic matter; a yellowish tinge was imparted to it by addition of potassic hydrate, but it did not reduce cupric salts.

After treatment with water, the gun-cotton was carefully exhausted with the usual mixture of ether and alcohol, and was found not to furnish a higher proportion of extract than the original material. The remainder of this sample, after further exposure in the bulb-tube for two years (*i.e.*, upwards of three years from the commencement of the experiment), had not altered in appearance, and was found to be in the following condition.

There was scarcely any perceptible odour in the tube on removing the extremity from the mercury; and the gun-cotton itself, when extracted from the bulb, had decidedly less odour than when examined two years previously. It was still highly explosive, and the toughness of its fibre had very slightly diminished. Water extracted only 1·3 per cent. of soluble matter; the extract had a faint acid reaction; a minute quantity of nitric acid was detected in it, but no oxalic acid; and it exerted to a very slight extent a reducing action upon cupric salts. The gun-cotton yielded 25·5 per cent. of soluble product to the mixture of ether and alcohol.

Experiments 3 and 4.—It was considered very probable that the gradual metamorphosis sustained by gun-cotton upon exposure to sunlight would be attended by the disengagement of gaseous products, and that the rate of generation of these might furnish an indication of the comparative rapidity with which different specimens were affected. With this view two bulb-tubes, similar to those used in the experiments just described, were respectively charged with 15 grms. of air-dry gun-cotton of the same manufacture as used in the preceding experiments, and exhausted over mercury. A small quantity of water was afterwards passed up into one of the tubes, so as

to form a layer upon the mercury 3·5 millims. in height. These bulb-tubes were exposed in the middle of October, 1863, side by side, in the position already described.

During exposure to light for the first four (autumn and winter) months, the depression of the mercury was not considerable in either instance, but it was nearly twice as great in the bulb-tube which enclosed water as in the other (88 millims. in the latter and 31 millims. in the former). During the next six months (from spring to autumn) the depression was more considerable; but at the expiration of twelve months' exposure to strong daylight and sunlight, it was only 115 millims. in the dry bulb-tube, and 220 millims. in the bulb-tube enclosing water. During the ensuing winter months the development of gas was again very trifling, though it continued to be greater in the tube which enclosed water. After two years' exposure to light the mercury was expelled from this tube, but the depression of the mercury in the dry tube amounted only to 340 millims., and after the third year's exposure the extent of depression in the latter was 660 millims. Neither of the specimens had undergone any alteration in appearance after exposure for three years and four months. They were then removed from the bulbs, and the following were the results of their examination :—

Both were slightly altered in explosiveness and strength of fibre, and possessed a somewhat pungent odour. The gun-cotton from the dry tube yielded 0·77 p. c. of soluble matter to water, while that from the tube which enclosed water furnished 1·4 p. c. The soluble gun-cotton amounted to 27 p. c. in the former, and 39·7 p. c. in the latter. Both of the aqueous extracts were slightly acid, contained traces of nitric acid, and reduced cupric oxide slightly, but contained no oxalic acid. The reactions were most distinct with the extract from the gun-cotton preserved in the moist globe.

These four experiments show that—

1. Gun-cotton in an ordinarily dry condition undergoes very slow change indeed when freely exposed in closed vessels (either containing air or with air excluded) to strong daylight and to the light and heat of the sun; the effects upon the material, during upwards of three years' exposure, being to diminish its explosiveness somewhat by the reduction of a portion of the trinitrocellulose to lower cellulose-products. The

material, when purified by washing in alkaline water after this very severe exposure to light, is still gun-cotton possessing useful explosive properties, and exhibiting no greater tendency to change than the original material.

2. If the space in which the gun-cotton is enclosed be kept saturated with aqueous vapour, the substance undergoes decidedly more rapid and considerable change, though, even under these circumstances, gun-cotton prepared according to the system now in use is much less rapidly decomposed by severe exposure to light than has been the case with specimens of gun-cotton previously experimented upon.

Samples of gun-cotton which had been submitted to a less perfect purification than usual, afforded indications of being somewhat more affected by prolonged exposure to strong daylight and sunlight.* Gas was more rapidly and abundantly disengaged from them than from the one referred to in the previous experiments; the change which the gun-cotton had sustained at the expiration of about $2\frac{1}{2}$ years was not so great as that observed in the specimen which had been treated with the alkaline bath, but washed for a short time only. The specimen had only a very faint odour, its explosiveness and strength had not undergone any appreciable change; water extracted only 0·3 per cent. of soluble matter; a trace of nitric acid was detected in the extract, but no oxalic acid and no reaction upon cupric salts could be obtained. The proportion dissolved by ether and alcohol amounted to 16 per cent.

But none of these specimens, in the preparation of which the complete system of purification had not been pursued, were found to be as injuriously affected by very long-continued exposure to sunlight and bright daylight as was anticipated.

A sample (19·8 grms.) taken from a large quantity of gun-cotton which had been impregnated with 0·5 per cent. of sodic carbonate, was exposed to strong light in the same way as the preceding specimens. During six months (between August and March) only a very slight indication of alteration was obtained. The depression of the mercury amounted to 15 millims. at the end of that period. Soon afterwards gas was more abundantly evolved, the depression amounting to 133 millims. after ten months' exposure. After eighteen months' exposure the amount of depression was 324 millims., which had increased to 432

* Phil. Trans., part I, 1867, p. 190–192.

millims. when the sample had been exposed for two years. After the lapse of two and a half years the mercury had not been entirely expelled from the tube. The gun-cotton was not altered in appearance or toughness of fibre, nor did it exhibit any appreciable diminution of explosiveness. It had a slight odour and faint acid reaction; the aqueous extract amounted to 1·5 per cent. (a portion of which was due to soda); it contained no oxalic acid, a small quantity of nitric acid, and reduced cupric salt slightly; ether and alcohol extracted 10 per cent. of soluble matter. This sample had, therefore, suffered less change than any of the others. The disengagement of gas was manifestly due in part to the decomposition of the sodic carbonate, by small quantities of acid developed after a time by the exposure of the gun-cotton as described. This sample, after having been washed in water, exhibits no difference whatever in character from specimens of freshly prepared gun-cotton, in which the proportion of soluble cellulose-products is above the ordinary average.

The observations showing that the preservation of gun-cotton in an atmosphere saturated with moisture rendered it somewhat more prone to alteration by long-continued exposure to light, have been confirmed by other experiments still in progress, in which known quantities of moist and wet gun-cotton are exposed to light in confined spaces, in comparison with dry gun-cotton. Thus, in one of these experiments, 43·71 grms. of perfectly dry gun-cotton and 40·045 grms. of gun-cotton in a damp condition have been enclosed in large stoppered bottles and exposed side by side to strong daylight and sunlight. After the lapse of two (summer) months they were carefully dried and their weights determined. The sample which had been exposed to light saturated with water had lost 0·33 per cent., the weight of the dry sample indicated a loss of only 0·02 per cent. They were then again exposed in the wet and dry condition for four months; the total loss in weight of the sample exposed in a wet condition was then found to amount to 0·6 per cent., that of the dry sample only to 0·14 per cent. (after six months' exposure). A trifling oxidation at the expense of oxygen in the water, established by the agency of sunlight, is doubtless the cause of the slight but decided influence which, under these circumstances, water has been observed to exert upon the permanence of gun-cotton; an influence which is quite

opposed to that exerted by the presence of water in gun-cotton stored in the dark, or exposed to high temperatures, as will be presently demonstrated.

The statement made by De Luca,* that when once decomposition has been established in gun-cotton, resulting in the development of nitrous acid, the progress of the change cannot be arrested, is not borne out by the results of numerous observations made by me. Many specimens of gun-cotton which, by exposure to high temperatures (100° and 90° C.) or by very long-continued exposure to lower temperatures (50° to 65°), have suffered considerable change, resulting in the development of nitric peroxide and of other products, have been afterwards preserved in glass bottles, both tightly closed and partially open, and freely exposed to light for periods ranging from one to three years, without undergoing additional change. In a few exceptional instances, further decomposition has after a time been established by the influence of light; but in those the gun-cotton was impregnated to a considerable extent with free (nitric) acid. Such specimens, if then thoroughly washed, a slightly alkaline solution being employed in their first purification, have afterwards not been found, up to the present time, to exhibit any greater tendency to decomposition by exposure to light, than the original gun-cotton.

Part II.—Effects of Heat upon Gun-cotton.

The behaviour of gun-cotton under exposure even to comparatively high temperatures is subject to very considerable modifications, which may be in great measure determined by the conditions of treatment. Illustrations of this were obtained at an early period of these investigations, in experiments instituted with the view to ascertain the average temperature at which gun-cotton explodes.

The following is a summary of the observations made on this head.

Exploding-point of Gun-cotton.—The apparatus employed in the experiments on this subject consisted of a small air-bath fitted with a thermometer and closed with a mica-plate, having a little circular opening in the centre, through which the gun-

* Comptes Rendus, vol. lix, p. 487.

cotton might be introduced, and which was kept closed when not in use. The mode of operating was modified in various ways. In the first instance the gun-cotton was combed out into a very loose condition, and allowed to rest upon metal in the air-bath. The temperature of the latter was then raised very gradually from 15° C. to 204°, or 205° C. When the time occupied in the passage to the maximum temperature was two hours and upwards, the gun-cotton did not explode at all (in six experiments), but gradually became dark brown, quite friable, and deprived of all explosive properties. When a considerably shorter time (about one hour) was occupied in the attainment of the maximum temperature, the gun-cotton exploded on one or two occasions, but not until its temperature had reached 205° C.

In the next experiments, the gun-cotton was employed in very small compact masses, and, resting upon a wooden support, was exposed to a continuously increasing temperature. The passage from 15° C. to the exploding-point ranged in these experiments from forty-five minutes to two hours, and the temperatures indicated at the moment of explosion were 136°, 137°·5 (twice), 138°, and 138°·5.

Further experiments were instituted for ascertaining in what particular mechanical condition the gun-cotton exploded most readily and at most uniform temperatures. Ultimately the material was employed in the form of pieces of loosely-twisted strand about 20 millims. long, and its exploding-point was determined by first raising the atmosphere of the air-bath to 105° C., then allowing the specimen to fall upon a diaphragm of wire gauze in the air-bath, at once increasing the temperature as rapidly as possible, and carefully reading the thermometer until the explosion occurred. The temperatures indicated in eight observations were, 147°, 148°·5, 150°·5 (twice), 151° (three times), and 151°·5.

These last experiments, which appear the most trustworthy, indicate that the average temperature at which the gun-cotton explodes when in a condition most favourable to its rapid heating, is about 150° C. In two observations, in which the gun-cotton was in a very open condition, the temperature being raised more rapidly than usual, the explosions occurred when the thermometer indicated 145° and 143°·5 C.; and in the experiments preceding these, which were differently conducted,

compact gun-cotton being exposed to heat for a considerable time, the point of ignition ranged between 136° and 138°·5 C. Schrötter, Redtenbacher, and Schneider, in their report upon Von Lenk's gun-cotton, mention that 136° C. is the *lowest* temperature fixed by Von Ebner at which this material explodes.

Effects upon Gun-Cotton of Exposure to 100° C.

Pélouze and Maury, in their accounts of the effects of heat upon gun-cotton, describe several kinds or stages of decomposition, as occurring, or producible at will, by its exposure to a temperature of 100° C., and state that in every instance they found a few minutes' exposure to that temperature sufficient to produce a disengagement of nitrous vapours.

A large number of experiments has been instituted with gun-cotton prepared at Waltham Abbey and Stowmarket according to Von Lenk's direction, and also with some specimens of Austrian gun-cotton, with the view of ascertaining the effect upon them of exposure to 100° C. The gun-cotton was exposed to heat in sealed tubes and in open vessels arranged in different ways. The quantities operated upon and other conditions in the experiments were varied, as will be presently particularized, the objects contemplated being, in the first instance, to examine into the effects of exposure of gun-cotton to heat, and, afterwards, to ascertain if possible by what circumstances those effects might be subject to modification.

The following is a condensed account of the observations made.

I. *Experiments in Sealed Tubes.—a.*—Air-dry gun-cotton (coarse yarn, manufactured in 1863), enclosed in a stout glass tube hermetically sealed, was maintained at 100° C. in a water-bath. The tube was filled with deep orange vapours in about three hours. The vapours gradually diminished in intensity, after a time, until the gun-cotton was converted into a gum-like mass, the transformation occurring most rapidly at the upper end of the tube, where the water produced during the change condensed and returned, charged with acid, upon the gun-cotton. When the sealed tube was opened, after continuation of the heat for three or four days (seven hours daily), nitric oxide escaped under considerable pressure. Upon closing the tube again,

after the escape of gas, and continuing the application of heat, the gun-cotton was gradually converted into a black pitch-like mass. Repetitions of this experiment furnished closely similar results.

b.—A tube containing fine gun-cotton thread, manufactured in 1863, was exhausted and sealed. After four hours' exposure to 100° C., it exploded with great violence, tearing open the stout copper water-bath in which it was heated. Portions of unburned gun-cotton were scattered about. Another tube containing some of the same gun-cotton, was opened after seven hours' heating, to allow the gas to escape, and again sealed. On the second day, after heating for three or four hours, it exploded violently. Other experiments, made with carefully dried gun-cotton, furnished results quite similar to those obtained with the air-dry material.

c.—Fine gun-cotton thread was introduced into a tube sealed at one end; the other extremity of the tube was constricted, then exhausted and filled with nitrogen, these operations being repeated three times; the tube was afterwards sealed and heated to 100° C. in a water-bath. After forty-five minutes faint red vapours were observed. In another quarter of an hour the colour of the vapours was very deep; in a short time nitrous acid began to condense in the cool part of the tube. After continuing the heat for $1\frac{1}{4}$ hour longer, the coloured vapours had entirely disappeared. The gun-cotton had become highly bleached, and in the upper extremity of the tube it was partially converted into the gummy substance. Nitric oxide escaped when the tube was opened.

d.—A sample of gun-cotton impregnated with about 0·4 per cent. of alkaline carbonate, was exposed to 100° in an exhausted sealed tube, for the purpose of collecting the gases evolved. When the tube had been heated six hours daily for five days, it was opened under mercury, and the gas, which escaped under considerable pressure, collected. The tube was again closed and heated for two days, when gas was once more collected from it. The experiment was interrupted, after the gun-cotton had been further heated for two days, the tube being fractured by the effects of an explosion in its vicinity. The collected gases were found to consist of 50·2 per cent. of carbonic acid, 4·7 per cent. of nitric oxide, and 45 per cent. of nitrogen.

These experiments appear to indicate that nitric peroxide or nitrous acid is liberated by the first decomposition of the gun-cotton, and at once establishes a further destructive action upon the substance, becoming reduced to nitric oxide, nitrogen being eventually liberated by complete reduction of the latter.*

The extent of surface of gun-cotton presented to the action of heat, and of the liberated acid, evidently exerts, as might be anticipated, an important influence upon the change. The characters exhibited by the products of decomposition of gun-cotton obtained in these experiments were similar to those already described by other chemists, and have been referred to in the preceding parts of this paper.

II. *Experiments in vessels open to the Air.*—Several experiments, conducted with considerably larger quantities of gun-cotton than before employed, were made with the view of obtaining, at one time, several distinct data regarding the decomposition of gun-cotton at 100° C. Direct evidence was sought of the development of heat in gun-cotton upon continued exposure to that temperature. The period was carefully noted when decomposition was first indicated by the disengagement of nitrous acid, after commencement of the experiment. In some instances, the loss of weight sustained by the gun-cotton was determined at intervals (*e.g.*, at the close of six hours, or one day's exposure to heat), the nitrous acid contained in the vessel being first displaced.

The vessels employed in these experiments were globe-flasks fitted by means of perforated corks, with long narrow glass tubes, and in most instances with thermometers graduated from 100° C. upwards. The flasks were of a size to receive the gun-cotton in a compact condition, and the thermometer-bulbs were inserted into the centre of the mass. Continuous observations were made in safety during the experiments, through a small glass let into a wooden screen, which was placed in front of the water-bath containing the heated flask. The results† obtained indicated:—

(1) That sufficiently protracted exposure to 100° C. under conditions unfavourable to the rapid expulsion of the nitrous

* Similar results were observed in experiments differently conducted.

† For the details of these experiments, *vide* Phil. Trans., part I, 1867, p. 197.

acid developed by the first action of the heat upon the gun-cotton, ensures the complete destruction of the original properties of this substance, and its conversion into a variety of volatile and fixed products.

(2) That the rapidity and violence of the decomposition resulting from the combined action of heat and of the acid generated, is regulated by the quantity of gun-cotton operated upon.

(3) That the mechanical condition of the gun-cotton exerts an important influence over the rapidity of decomposition at 100° (a point also indicated by the results of experiments in sealed tubes).

(4) That a very important difference may exist between the behaviour of different samples of gun-cotton, even if operated upon in precisely the same manner, quantities, and mechanical conditions. This was especially illustrated by a comparison of results obtained in precisely similar experiments instituted with Austrian gun-cotton, several samples of which exploded after exposure for a short time to 100° C., and with samples of Waltham Abbey gun-cotton manufactured at different times, in not one of which was an explosion brought about by long-continued exposure of equal quantities (6·5 grms.) to 100° C. The Austrian samples differed very greatly in composition from all the products of manufacture prepared at Waltham, according to Von Lenk's system; and it will be shown presently that this circumstance may serve to account for the exceptional proneness of those specimens to very violent decomposition as demonstrated by these particular experiments.

It need perhaps scarcely be stated that the temperature-observations in these experiments (and others still to be described) were instituted more with the view to afford a good means of registering the comparative rapidity of decomposition of different specimens of gun-cotton operated upon under equal conditions, than with the idea of attempting to ascertain the actual moment of development of heat and progressive rise of temperature in a mass of gun-cotton. Such observations could only be correctly made with much larger quantities of material, so confined as to prevent the escape of heat from the interior, and are therefore impracticable on the score of danger. A considerable number of these thermometric observations, which unquestionably recorded close approximations of the actual rise in temperature of the interior of the mass of badly

conducting gun-cotton, showed that, when the temperature passes 110° to 112° C., the development of heat proceeds with great rapidity, so that very speedily the rise of the thermometer does not keep pace with the heating of portions of the gun-cotton in close proximity to it, and therefore the explosion of the mass appears to occur at a temperature considerably lower than the actual exploding point of gun-cotton.

In continuation of the heat-experiments, several samples of gun-cotton from Waltham Abbey and Stowmarket, weighing 3 grms. each in an air-dry condition, were exposed to 100° C. in conical assay flasks, into which long quill-tubes were fitted, the operations being conducted in a precisely similar manner in eight experiments.

The results obtained* point to very important differences in the powers of different specimens of gun-cotton to resist destruction by exposure to 100° C. Of five samples manufactured at Waltham Abbey, only one exhibited the effects of such exposure described by Pélouze and Maurey as invariable, namely, the disengagement of nitrous vapours within a few minutes. One specimen did not exhibit this sign of change until after five hours' exposure, and then only to a very slight extent. Of two specimens of gun-cotton from Stowmarket, one decomposed with very considerable rapidity at 100° C., and the other did not, in one experiment, evolve any visible amount of nitrous acid during forty-five hours' exposure, in nine days, and exhibited very slight signs of change at the expiration of this severe treatment; while in a second experiment, with a portion of the same sample, slight decomposition became apparent at the close of the third day's exposure for five hours.

The cause of the latter difference in the behaviour of one and the same sample, upon different occasions, was traced to the circumstance that the specimen, in the condition in which it was first employed, contained a somewhat larger proportion of moisture than when the experiment was repeated with it, in consequence of its having been in a damp locality for a short time before the first portion was operated upon. Thus one possible reason for the different behaviour of several samples of gun-cotton prepared by one and the same process was indicated. In confirmation of the influence exerted by moisture in retarding the decomposition of gun-cotton exposed to a high tempera-

* Phil. Trans., part I, 1867, p. 199.

ture, the results of a preliminary experiment may be here recorded, which was instituted with a sample of gun-cotton found to be very readily affected by exposure to heat.

Three specimens, each of one grm., were exposed side by side in small, long-necked flasks to 100° C., in three different conditions. The one was air-dry (and contained therefore about 2 per cent. of water), the second was dried immediately before the experiment by sufficient exposure to 50° C., and the third was saturated with water and pressed between bibulous paper. The dry sample showed signs of decomposition in ten minutes, the air-dry sample began to decompose in forty-five minutes, and the moistened specimen exhibited no acidity after exposure to 100° C. five hours daily for three days (further experiments on the protective power of water will be presently described). In all subsequent experiments upon the comparative effects of exposure of different samples to elevated temperatures, the gun-cotton was employed in a dry condition.

The discrepancies noticed above in the behaviour of different samples of gun-cotton under exposure to 100° C., led to a searching investigation into the composition of products of manufacture obtained from Waltham Abbey, Stowmarket, and Hirtenberg, the results of which were laid before the Royal Society last year.*

It was established by this inquiry that gun-cotton manufactured at those establishments contains variable proportions of the following substances, foreign to the most explosive gun-cotton, *trinitrocellulose*, or $C_6 \overset{H_7}{3NO_2} O_5$.

(1) Hygroscopic moisture, the proportion of which amounts very uniformly to about 2 per cent., except in special instances, when mineral impurities in the material exert an influence upon its hygroscopic properties.†

(2) Mineral matters, varying in amount with the character of water used in purifying the material, with the duration of its treatment with water, and with the circumstance whether the purified gun-cotton has been submitted to the treatment with soluble glass, recommended by Von Lenk. These mineral

* Journal of Chem. Soc., vol. v, p. 310.

† Several of the earlier products of manufacture obtained at Stowmarket were found to absorb from the atmosphere, under ordinary conditions, from 0·5 to 1·5 per cent. more moisture than the average proportion (2 per cent.) contained in Von Lenk's gun-cotton.

matters include calcic and magnesian carbonates, silica, clay, and occasionally small quantities of sand and alkaline salts.

(3) Products of the less complete action of nitric acid upon cellulose, the nature of which has been investigated by Hadow. These products, which are less explosive than trinitrocellulose, and are more or less readily soluble in mixtures of ether and alcohol, were found to exist in very considerable proportion in some samples obtained from Hirtenberg and Stowmarket, and have also been found to the extent of about 2 per cent. in the most perfect products of manufacture. Their formation may be due to insufficiently protracted treatment of the cotton with the mixed acids, to the employment of acids of insufficient strength, and to the presence of hygroscopic moisture in the cotton at the time of its conversion. An elevation of temperature during the treatment of the cotton with the acids would also give rise to the production of soluble gun-cotton.

(4) Products of the partial oxidation, by nitric acid, of organic impurities existing in the cotton, even after the preliminary purification to which it is subject. These products, which are formed from portions of seed-husk adhering to the cotton, and from small quantities of gum-like and other substances still retained within the fibre, escape complete removal from the gun-cotton, although the larger proportion passes into solution during the treatment with acids and upon the subsequent digestion in an alkaline bath. The proportion of these substances, existing in the finished gun-cotton, varies with the description and quality of cotton employed, with the duration of the digestion in acids, and the degree of perfection of the purifying processes to which the material has been submitted. They are discovered by treatment of the gun-cotton with alcohol, and no specimen has yet been examined by me which has been found entirely free from them, while comparatively considerable proportions have been found to exist in a few specimens from Hirtenberg and Stowmarket. A description of the nature of these impurities, as far as it could be determined, has been given in the previous memoir*.

It has been argued by Schrötter, Redtenbacher, and Schneider, in their official report upon Von Lenk's gun-cotton, that an incomplete conversion of cellulose into the most

* Transactions Royal Society, vol. clvi, p. 285.

explosive gun-cotton may be one cause of the want of stability observed in the early products of manufacture (at Bouchet, &c.); and consequently the existence in gun-cotton of a proportion of the third class of impurities above specified should, according to these chemists, give rise to, or promote a tendency to spontaneous change in the material. On the other hand, Pélouze and Maurey consider it probable that a gun-cotton will be the more liable to spontaneous change the further it is removed in composition from the cellulose type, and that products prepared by prolonged immersion in large proportions of very concentrated acids will therefore be more liable to spontaneous ignition than the gun-cotton prepared by a brief immersion in less concentrated acids. No experimental data are given in support of either opinion.

The discordant results furnished by the heat-experiments just referred to, and the facts established by investigating the composition of the gun-cotton operated upon, led to the institution of a very considerable number of experiments with the view of ascertaining, if possible, whether the establishment of change in gun-cotton by its exposure to high temperatures has to be ascribed to the instability of trinitrocellulose itself, or whether it is to any extent due to the injurious influence of less permanent bodies existing as impurities in the ordinary product of manufacture.

A careful comparative examination was instituted of the effects of exposure, under equal conditions, to 100° C. upon thirty-six different samples, (from Waltham Abbey, Stowmarket, and Hirtenberg,) in portions of which the matters soluble in ether and alcohol had been determined. One gramme of each sample was first dried in a water-bath at a temperature of 50° C.; it was then introduced loosely into a small flask having a neck about 220 millims. in length, and immersed in boiling water, the first indications of the disengagement of nitrous acid being afterwards carefully noted. The specimens were uniformly exposed to 100° C. for thirty hours (six hours daily for five consecutive days), unless, as was the case in a few instances, the gun-cotton had suffered complete change within a shorter period.*

The following are the principal facts demonstrated by the foregoing experiments:—

* *Vide* Phil. Trans., part I, 1867, p. 202, for details of experiments.

1. The results furnished by the samples of Waltham Abbey gun-cotton demonstrate that different samples of the material, manufactured as far as possible in the same manner, are not alike affected by exposure for a fixed period to 100° C. under uniform conditions. Of thirteen samples of Waltham Abbey gun-cotton, four resisted in a remarkable manner the destructive effects of heat, and remained unchanged in physical properties and explosiveness after thirty hours' exposure to 100° C. This treatment only developed acid to a slight extent in these particular samples; but in the other nine specimens it produced somewhat greater alteration; nitrous acid was disengaged in more considerable proportions, the fibre of the gun-cotton was rendered more or less rotten, and its explosiveness was diminished in different degrees.

2. The comparative celerity with which nitrous acid is disengaged from different specimens of gun-cotton upon exposure to 100° C., does not afford a reliable indication of their relative susceptibility to rapid decomposition at that temperature. The following results illustrate this point:—Some specimens of Waltham Abbey gun-cotton which exhibited uniform powers of resisting the destructive effect of heat furnished the first faint indications of development of acid vapours in one hour, four hours, and fourteen hours, respectively, after first exposure to 100° C. Three samples which were altered alike, and slightly, by uniform exposure to 100° for thirty hours, exhibited the first symptoms of decomposition at $1^h\ 20^m$, $2^h\ 30^m$, and four hours after commencement of the experiment. Again, a sample which exhibited no sign of change beyond slight acidity at the close of the experiment afforded faint indications of the development of acid in one hour, while another specimen which sustained comparatively considerable change did not involve any acid vapour until four hours after its first exposure to heat. Out of thirteen samples obtained from Stowmarket, five did not furnish signs of disengagement of acid vapours until after the lapse of five hours and upwards, while among an equal number of Waltham Abbey samples only three furnished no signs of change for four hours and upwards. On the other hand, these samples of Waltham Abbey gun-cotton were, after thirty hours' exposure, only very slightly affected, while the Stowmarket samples just referred to, all exhibited important signs of change.

A careful examination into the possible causes of these differences showed that they were to be ascribed, at any rate in very great measure, to variations in the proportion and character of the mineral matters contained in the specimens. Some few of the Waltham Abbey samples contained larger proportions of calcic and magnesian carbonates (deposited upon the fibre by the hard water in which the material had been washed) than other samples. There was consequently present in such specimens a larger amount of matter capable of neutralizing acid, if liberated by the action of heat, than in others; and therefore the period would be proportionately delayed, in those instances, when the development of free acid would first become evident. The Stowmarket samples had been submitted to the "silicating" process, and the chief result of this treatment is the deposition of small proportions of alkaline and earthy carbonates upon the fibre, in addition to what it would acquire by simple long-continued exposure to running water. This circumstance tends to explain why the Stowmarket gun-cotton experimented with, though generally much more seriously affected by protracted exposure to 100° C. than the Waltham Abbey samples, appeared to resist change in several instances for much longer periods than the latter.

The proportion and nature of the mineral matters in gun-cotton may therefore exert a very notable effect upon the behaviour of the material when exposed to high temperatures. Moreover, the results of subsequent experiments have demonstrated most decisively that the influence which the presence of earthy or alkaline carbonates, mechanically distributed in small proportion through a mass of gun-cotton, exerts upon the effects produced by exposure to heat, is in many instances not confined to a simple delay of the *indications* of change furnished by the development of acid; it may also manifest itself by actually retarding and even considerably limiting, if not altogether preventing, the spontaneous decomposition of the gun-cotton itself. These effects are of such evident importance in connection with the question of the stability of gun-cotton, that they have been made the subject of extensive experimental inquiry, the results of which will be given under a special head.

3. The different behaviour of the samples of gun-cotton operated upon in the experiments under discussion, cannot be ascribed to differences in the *proportions* of matter soluble in

ether and alcohol present in them. Thus, four samples which withstood to the greatest extent the action of heat, contained 1·8, 2, 2·1, and 2·31 per cent. of soluble matter, which numbers represent the lowest, the mean, and almost the highest proportions of soluble matter in the Waltham Abbey gun-cotton. Again, some samples of Waltham Abbey products, containing identical proportions of soluble matter, behaved very differently on exposure to 100°. The want of connexion between the proportion of matter soluble in ether and alcohol, and the stability of the sample was even more strikingly demonstrated by results obtained with specimens of Stowmarket and Hirtenberg products. Samples containing equal proportions of soluble matter behaved very differently, while others, in which the amount of soluble matter differed very considerably, behaved alike, upon exposure to heat.

4. A comparison of the *characters* exhibited by the matters which ether and alcohol extracted from different samples employed in these experiments, appeared to throw much greater light upon the causes of their different behaviour, than the comparison of the *proportions* of soluble matter which they furnished. Reference has already been made to the matters soluble in alcohol alone, which have been discovered in small but variable proportions in all samples of gun-cotton hitherto examined. Both the quantity and character of these substances extracted from different specimens of gun-cotton exhibit variations, as might be anticipated, when it is remembered that they are derived from impurities retained by the cellulose to an extent determined by the particular description and degree of purity of the cotton operated upon. In the Waltham Abbey specimens employed, the proportion of matter varied only slightly (between 0·72 and 0·9 per cent.); yet, although the comparatively slight differences in the effects of heat upon the different samples were in part ascribable to variations in the proportions of mineral matters present, indications were obtained that the gun-cotton which resisted the action of heat to the greatest extent contained the smallest proportion of nitrogenized organic matter not derived from cellulose. The Stowmarket samples afforded much more decided evidence of the influence of these foreign products upon the stability of the gun-cotton. Two specimens from which nitrous acid-vapours were disengaged within ten minutes of their first exposure to 100° C., and three others which,

owing apparently to the influence of mineral matters, did not furnish acid-vapours until after five hours' exposure, yielded extracts with ether and alcohol decidedly different in character from the other specimens; a comparatively large proportion consisted of nitrogenised acid matter of a resinous character, soluble in alcohol.

With two or three exceptions, the samples of Austrian gun-cotton exhibited decided signs of less complete purification of the cotton previous to conversion, than the generality of samples of English manufacture. It should also be observed that the extract by ether and alcohol after treatment of the samples with alcohol, possessed in several instances the characters of photographic collodion (the solutions furnishing tough transparent films upon glass), which was not the case with any of the specimens of Waltham Abbey gun-cotton, and in only one or two instances among the samples from Stowmarket. The ordinary ethereal extract from the English samples furnished a horny brittle residue, contracting greatly upon perfect desiccation, and appearing to consist chiefly of the product "B" described by Hadow as having the formula $C_{18}H_{22}O_{15}8NO_2$. No decided evidence was, however, obtained in support of the conclusion that this difference in the character of the *ethereal* extract affected the stability of the gun-cotton.

The destructive effect upon the structure of the fibre produced by the long-continued digestion of the gun-cotton in warm solvents, which is necessary for ensuring the extraction as completely as practicable of the soluble matters, renders it very difficult to obtain reliable indications of the effects of heat upon gun-cotton deprived of those substances. The following experiments appear, however, to afford considerable support to the inference drawn from some of the results of the heat-experiments just referred to, that the existence in gun-cotton of small proportions of organic impurities, resulting from partial oxidation of foreign matters enclosed in the cotton-fibre exerts a very prejudicial influence upon the stability of the material, and that there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose-products, when associated in small or large proportion with trinitrocellulose.

Four specimens of gun-cotton were extracted with ether and alcohol, by being twice digested for periods of 24 hours, in a considerable volume of the mixture, and afterwards washed.

The dry specimens were then exposed for twelve hours (in two days) to 100° C., side by side with portions of the original samples.

The results* showed that one sample, which contained the average proportion of matter soluble in alcohol existing in Waltham Abbey gun-cotton, and a comparatively very small proportion of matter soluble in ether and alcohol, was rendered very much less susceptible of change at 100° C., by extraction with the mixed solvents, while the other three, apparently in consequence of the injury to the structure of the fibre resulting from the extraction of a comparatively considerable proportion of imperfectly converted gun-cotton by the ether and alcohol, were rendered somewhat more prone to change by the treatment received.

Two specimens of gun-cotton, selected from those which in preceding experiments had been found most susceptible of decomposition at 100° C., were digested for some time in dilute acetic acid, afterwards thoroughly washed, first in slightly alkaline water, and then in distilled water. By this treatment such mineral impurities as might have an influence upon the rapidity of decomposition of the gun-cotton were removed. One-half of each sample was digested for 24 hours with ether and alcohol, afterwards washed with the mixture and dried. The samples thus treated were exposed to 100° C. in a water-bath, side by side with corresponding quantities of the same specimen which had simply been extracted with acetic acid. The results observed were as follows:—

	No. 1.		No. 2.	
	Treated with acetic acid only.	Treated with ether and alcohol.	Treated with acetic acid only.	Treated with ether and alcohol.
Indications of change observed after first exposure to 100° C.	35 minutes.	7½ hours (3 hours on the second day).	30 minutes.	3h 45m, very faint.
Loss of weight after 4½ hours' exposure to 100° C.	17·9 per cent.	2·3 per cent.	20 per cent.	1 per cent.

* Phil. Trans., part I, 1867, p. 206.

The very marked difference in the stability of these specimens (which contained only very small proportions of soluble gun-cotton), when exposed to 100° C. in the two different conditions, appears to afford strong evidence that the abstraction of the matters soluble in ether and alcohol greatly increases the stability of the gun-cotton. The next following experiments show, on the one hand, that this difference does not appear ascribable to the removal of the soluble gun-cotton from the trinitrocellulose, and indicate, on the other hand, that the closing up of the fibres resulting from the solution (or gelatinization), but imperfect removal from the gun-cotton of the soluble portions may, in the above experiment, have imparted to the material increased powers of resisting decomposition at a high temperature.

Four specimens of gun-cotton, containing small proportions of imperfectly converted material, were thoroughly saturated with a very weak solution of pure soluble gun-cotton (or collodion), then at once removed from the liquid and dried. The mechanical condition of the gun-cotton was not perceptibly altered by this treatment. These specimens were exposed to 100° C., together with portions of the original samples (all of them being for this purpose packed lightly and uniformly in small flasks). In every instance the prepared gun-cotton resisted the action of heat for a much longer period than the unprepared material. The addition, therefore, of less perfectly converted gun-cotton to the ordinary product did not have the effect of promoting its decomposition at 100° C.; on the contrary, when applied as indicated above, it evidently renders the material considerably less susceptible of change, probably because the fibres are partially sealed, or in some other way mechanically protected by the treatment with dilute collodion. That the partial or complete closing of the fibre does exert an important influence upon the power of gun-cotton to resist the action of heat, was demonstrated by another experiment, in which a sample of dry gun-cotton was allowed to remain for 18 hours in a confined space together with an open vessel containing the ether- and alcohol-mixture. It was afterwards dried and exposed to 100° C., side by side with a portion of the sample in its original condition. The latter exhibited signs of decomposition within two hours; the sample which had been exposed to the action of the vapour only exhibited faint signs of change after 18 hours' exposure.

A specimen of Waltham Abbey gun-cotton was in the first instance digested with dilute acetic acid and thoroughly washed, the object of this treatment being to remove any mineral matters from the sample which might exert a neutralizing action and thereby influence the effects of exposure to heat. One half of this gun-cotton was then digested for two days with warm alcohol, and was afterwards repeatedly washed. A small portion of the dry gun-cotton thus purified was heated to 100° C. side by side with some of the same specimen which had only been extracted with acetic acid. Early on the second day of the experiment, the latter specimen began to evolve nitrous acid; and about thirty minutes afterwards the sample extracted with alcohol exhibited faint signs of decomposition.

Eight grammes of each of these samples, and a similar quantity of the gun-cotton in its original condition, were afterwards introduced into very long-necked flasks, the openings of which were loosely closed with corks and exposed for six days, seven hours daily, to 65° C.; as none of the specimens exhibited any sign of change at the expiration of that period, the temperature of the water-bath was maintained at between 88° and 90°. After about nine hours' exposure to this temperature, the original gun-cotton began to decompose, and two hours later an extremely faint indication of nitrous acid was observed in the sample extracted with *acetic acid*. After two days' (twelve hours) further exposure to heat, the first signs of decomposition became apparent in the flask containing the sample which had been extracted with *alcohol*. The coloration of the atmosphere continued, however, to be only faint in the flasks containing both extracted specimens during ten days' exposure to about 90°.

The observation made in this experiment, that the treatment of the gun-cotton with acetic acid decidedly increased its power of resisting the destructive effects of heat, was quite at variance with the anticipated result; for it was considered that the treatment of ordinary gun-cotton with the acid, if it in any way influenced the subsequent action of heat upon the material, would have an accelerating effect, in consequence of the absorption of earthy carbonates; several additional experiments* confirmed, however, the correctness of the above observations.

Upon examining the extract obtained by digesting gun-

* Phil. Trans., part I, 1867, p. 210.

cotton with acetic acid in the cold, it was found to contain a small quantity of organic matter of resinous character, insoluble in water, but soluble in alcohol alone and in ether and alcohol, containing nitrogen and deflagrating when heated; it was evident, therefore, that this treatment of gun-cotton had the effect of purifying it to some extent from the organic impurities more perfectly removed by the extraction with alcohol.

The treatment of gun-cotton with dilute hydrochloric acid was not found to effect the removal of any proportion of these organic impurities, while the carbonates were, of course, readily extracted thereby. When gun-cotton, thus purified and very thoroughly washed, was exposed to heat side by side with the material in its original condition, the latter exhibited decidedly greater power of resisting change, thus furnishing an important indication of protective power exerted by carbonates if present in gun-cotton, which will be presently examined into more fully.

It is considered that the foregoing experiments afford good grounds for the following conclusions:—

(1) That the invariable existence in gun-cotton of small proportions of organic impurities, resulting from the partial oxidation of foreign matters enclosed within the cotton fibre, exerts a very prejudicial influence upon the stability of trinitrocellulose.

(2) That there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose-products, when associated in large or small proportions with trinitrocellulose.*

Exposure of Gun-cotton to 90° C.

It is stated by Pélouze and Maurey that, in their experiments, the exposure of gun-cotton to 90° furnished identically the same results as those produced by the temperature of 100° C., excepting that the phenomena of decomposition, instead of appearing after a few minutes, only became manifest after several

* The latter conclusion received great support from experiments, some of which were upon a considerable scale, instituted with the less explosive, soluble, varieties of gun-cotton, which has been manufactured at Waltham Abbey (*vide* Phil. Trans., part I, 1867, p. 210).

hours. This statement has been confirmed, by the results of comparative experiments* which I have instituted at 90° and 100°, to this extent, that in all instances the first signs of change become manifest in the specimens heated to 100°; that sometimes the interval of time between the first exposure to heat and the first indications of decomposition is much greater at the lower than the higher temperature; and that, in most instances, the decomposition of the gun-cotton was not only slower, but also much less serious at 90° than at 100°. Exceptional specimens, exhibiting either a very unusual want of stability (*e.g.*, some of the specimens from Hirtenberg and Stowmarket which have already been referred to), or a remarkable power of resisting decomposition at 100°, generally showed but little difference in behaviour when subject to the influences of the two temperatures.

Exposure of Gun-cotton to Temperatures ranging from 50° to 60° C.

Several experiments, corresponding in their nature to those described in the first part of the account of the action of light upon gun-cotton, have been instituted for the purpose of obtaining data regarding the influence upon the material of very long-continued exposure to the above-named temperatures. The air-dry gun-cotton was introduced into large bulbs blown at the extremities of barometer-tubes, the latter being placed with their openings over mercury and exhausted in the manner already described, so that the height of the mercury-column in these tubes, at the commencement of the experiments, was very nearly that of the barometer at the time. Sufficient gun-cotton (from 14 to 20 grammes) was employed to fill the globes pretty compactly. The bulbs were enclosed in metal water-baths, in which they were always perfectly surrounded by water maintained for definite daily periods at a constant temperature by gas-flames, accurately adjusted by self-acting regulators. Daily observations were made, before heat was again applied, of the height of mercury in the tube (with the necessary corrections), of the appearance of the gun-cotton through the glass, and of any other points worty of note.†

* *Vide* Phil. Trans., part I, 1867, p. 212.

† For details of experiments, *vide* Phil. Trans., part I, 1867, p. 213.

In one experiment 20 grms. of perfectly dry Waltham Abbey gun-cotton, representing the ordinary product of manufacture, was exposed in a bulb-tube exhausted over mercury to 65° C., for seven hours daily. The mercury-column was very gradually depressed, as in the preceding experiments with gun-cotton of this kind, and after the experiment had continued for ten weeks, gas escaped from the opening of the tube. In about one week more, sufficient gas was collected for examination; it was found to consist of—

Carbonic acid	45·6	per cent.
Nitric oxide	10·8	„
Nitrogen	43·5	„

Some water had become deposited in the sides of the tube, and a small quantity of mercurous nitrite had formed. The application of heat to the tube was continued with the view of obtaining a further quantity of gas, but the experiment was carried on uninterruptedly for a further period of nearly twelve months before a sufficient amount (about 150 cub. centims.) could be collected. This second product contained—

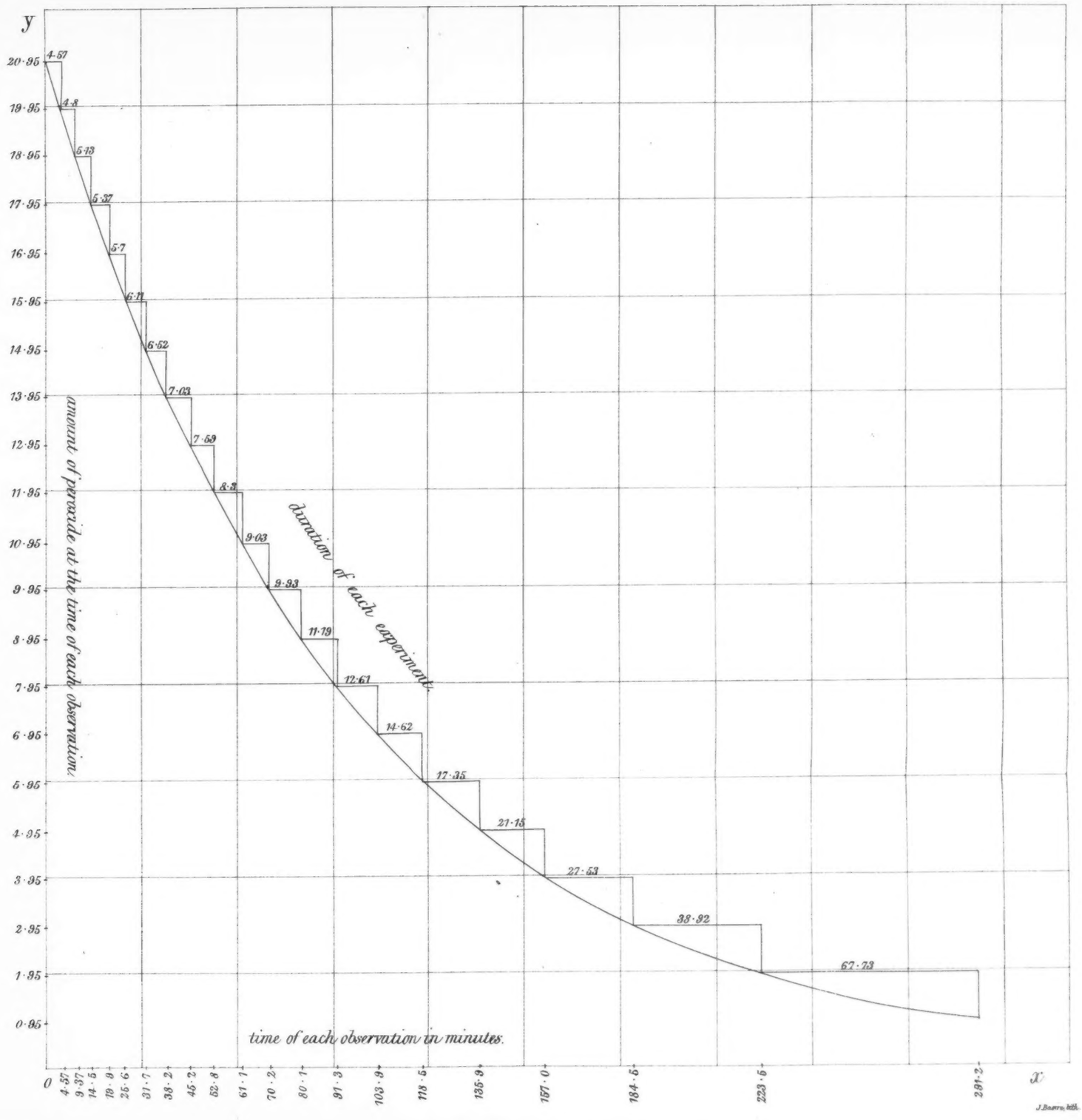
Carbonic acid	55·7	per cent.
Hydrogen	6·4	„
Carbohydrogen	traces.	
Nitric oxide	2·1	„
Nitrogen	35·7	„

The total volume of gas evolved during fourteen months' exposure of the gun-cotton to 65° C., for seven hours daily, was about 660 cub. centims.

On removing the specimen from the bulb-tube, it exhibited no alteration in colour, appearance, or explosiveness; the strength of fibre had slightly diminished; nitric acid was detected in small quantity in the aqueous extract, but no oxalic acid. A very slight reducing action was exerted upon cupric salts, but the proportion of matter soluble in ether and alcohol had not appreciably increased. At the conclusion of the experiment the specimen was washed in slightly alkaline water, dried, and exposed to strong daylight and occasional sunlight, in a stoppered bottle. Up to the present time (after nine months' exposure) the specimen has suffered no change whatever.

It would appear from these experiments, which were always commenced *in vacuo*, but continued after a short time in an atmosphere of the gaseous and volatile products formed, that gun-cotton, prepared and purified according to the system now in use, manifests some slight but undoubted symptoms of gradual change, if maintained for several hours at as low a temperature as 55° C. in a confined space;—that a very long-continued exposure to that temperature does in some instances produce a notable alteration in the composition and explosive properties of the substance;—that a similar change is somewhat more rapidly developed if the gun-cotton be exposed to temperatures of 60° and 65°; but that the exposure of the substance several hours daily, even for months, to the highest of those temperatures does not so seriously affect the ordinary products of manufacture as to prevent their being afterwards restored, by the ordinary process of purification from acid, to a condition differing but little, practically, from that of the original material. These experiments were instituted with comparatively considerable quantities of gun-cotton (14–20 grms.), but it must be at once admitted that, if the material were exposed in large compactly packed masses (5–10 kilos.) to the temperatures ranging between 55° and 65° for the periods given in the preceding experiments, it would be more seriously affected, and that the changes which would ultimately be developed by the free acid accumulating in the gun-cotton might give rise to spontaneous heating of the mass. On the other hand, it must be borne in mind that even the lowest of those temperatures occurs in nature only under exceptional circumstances, *and for brief periods.*

It may perhaps be considered that the arrangement of heating the gun-cotton over a column of mercury, adopted in the foregoing experiments with the view of obtaining continuous records of the progress of change, was of a nature somewhat favourable to the material operated upon, because a small surface of mercury was exposed to direct contact with the gases or vapours evolved, and might, by its own oxidation, remove a portion of the generated acid which would otherwise have reacted injuriously upon the gun-cotton. It has indeed been stated, in the description of the experiments, that a few crystals of mercurous salt were always formed upon the exposed surface of the mercury, the production of the salt being favoured by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7·03
7·59
8·3
9·03
9·93
11·19
12·61
14·62
17·35
21·15
27·53
38·92
67·73
amount of pressure at the time of each observation.
duration of each experiment.
time of each observation in minutes.
0
4·57
9·37
14·5
19·9
26·6
31·7
38·2
45·2
52·8
61·1
70·2
80·1
91·3
103·9
118·5
135·9
157·0
184·5
223·6
291·2
x
J.Basire, lith.

the condensation over the metal of a small quantity of water, produced as the experiment proceeded. But it must be borne in mind that the surface of mercury exposed was always very small (only from 78-100 sq. millims.), while the quantity of cotton operated upon was considerable, and that, between each consecutive period of exposure to heat, the gun-cotton absorbed, as it cooled during the night, the water impregnated with acid which had been previously expelled from it. Experimental proof* was, however, obtained that ordinary gun-cotton, when exposed to 65° in vessels not closed by mercury, and so arranged that any liberated acid would not escape from contact with the material, was somewhat more rapidly and seriously affected than was the case in the globe-experiments.

The protracted exposure of air-dry gun-cotton to a temperature ranging between 60° and 55° in a vessel *to which air had access*, did not effect any greater alteration in the material than was observed in the globe-experiments. Thus 53·968 grms. of air-dry gun-cotton, after exposure to heat seven hours daily for ten days, weighed 53·902 grms.; after a further exposure for seven days it weighed 53·882 grms., and after a third exposure for five days it weighed 53·881 grms. The sample had therefore only sustained a loss of 0·10 per cent.

Two other specimens, weighing 44 and 34 grms., were exposed day and night in a hot-air chamber, to a temperature ranging between 35° and 50°. The specimens were weighed periodically, in an air-dry condition. After the lapse of ten weeks one sample had lost 1·18 per cent., and the other 1·56 per cent.

In conducting these quantitative experiments, it was observed that the exposure of gun-cotton for a protracted period to a moderately elevated temperature had the effect of reducing the hygroscopic power of the fibre, so that upon exposure of gun-cotton which had been thus heated to the atmosphere, the maximum proportion of moisture absorbed by it was very notably lower than that contained in the original sample. The actual loss sustained by the above samples, which were always weighed after exposure to air for definite periods, was therefore somewhat less than indicated by the numbers given.

* Phil. Trans., part I, 1867, p. 217.

PART III.—INFLUENCE EXERTED UPON THE STABILITY OF GUN-COTTON BY SPECIAL MODES OF PREPARING AND PRESERVING IT.

I. *Reduction of Gun-Cotton Fibre to a fine state of Division.*—Abundant proofs have been obtained that the long-continued washing and the treatment with an alkaline liquid to which gun-cotton is submitted, do not completely separate from it products of the partial oxidation of organic impurities retained by the cotton up to the time of its conversion. This is unquestionably due in great measure to the tubular structure of the fibre. If the impurities were merely upon the surface of the fibre, their perfect removal by the action of solvents should be accomplished without difficulty, but it does not appear that even long-continued digestion of gun-cotton in alcohol has the effect of completely freeing it of the impurities soluble in that liquid which are locked within the fibre. The action of a warm or cold alkaline liquid upon the material might perhaps eventually result in the complete removal of those bodies; experiments have, however, proved that the loss of product and destructive effect upon the fibre, resulting from any other than a brief digestion in a very dilute alkaline bath, are too considerable to admit of such a treatment.

But though the treatment of gun-cotton with warm alkaline baths cannot be advantageously extended, satisfactory proof has been obtained that the stability of gun-cotton which has been purified as far as is possible by the present system, may be importantly increased by submitting the material to a special process of washing.

In the experiments instituted upon the application of gun-cotton as a substitute for gunpowder, some very advantageous results have attended the conversion of the material into homogeneous masses of any desirable form or density, by preparing it according to the method commonly employed for converting rags into paper. In reducing the material to a very fine state of division by means of the ordinary beating- and pulping-machines, the capillary power of the fibres is nearly destroyed, and the gun-cotton is, for a considerable period, very violently agitated in a large volume of water. It would be exceedingly difficult to devise a more perfect cleansing process than that to

which the gun-cotton is thus submitted; and the natural result of its application is that the material thus additionally purified acquires considerably increased powers of resisting the destructive effects of heat. Samples of the pulped gun-cotton, even in the most porous condition, have been found to resist change perfectly upon long-continued exposure to temperatures which developed marked symptoms of decomposition in the gun-cotton purified only as usual. The pulping process applied to gun-cotton affords, therefore, important additional means of purifying the material, the value of which may be further enhanced by employing a slightly alkaline water in the pulping-machine.

II. *Impregnation of Gun-cotton with substances capable of neutralizing free acid.*—The slightest change sustained by gun-cotton is attended by the development of free acid, which, if it accumulates in the material, even to a very trifling extent, greatly promotes decomposition. Numerous experimental data have been collected with respect to the establishment and acceleration of decomposition in gun-cotton exposed to light or elevated temperature by free acid, which either is present in the imperfectly purified material, or has been developed by decomposition of gun-cotton or its organic impurities.

Samples of gun-cotton which, by exposure to elevated temperatures or for considerable periods to strong daylight, had sustained changes resulting in a considerable development of acid, have afterwards been thoroughly purified by washing and exposed to light for months, and in some instances for two and three years (up to the present time) without undergoing further change, while corresponding samples, confined in closed vessels without being purified, have continued, in some instances, to undergo decomposition, and the original substance has been completely transformed into the products repeatedly spoken of. Instances have, however, occurred in these experiments in which gun-cotton has resisted further change, even under these circumstances.

Gun-cotton, purified as usual, has been confined in stoppered glass bottles, having previously been rendered slightly acid with nitric acid. In these instances the gun-cotton has always undergone decomposition upon exposure to light, the rapidity of its change varying with the quality of the material. Other specimens have been introduced into well-stoppered bottles,

nitric peroxide being then passed into them for a short time, and the bottles afterwards tightly closed and placed in a dark cupboard. The gas was rapidly absorbed by the gun-cotton, which assumed a green tinge and gradually contracted, the colour of the vapours in the bottles slowly becoming deeper again. After the lapse of two months the samples had contracted into compact masses, occupying less than one-fourth the original volume; they were coloured green, and dark orange vapours filled the vessels. From this period the nitric peroxide diminished in quantity very gradually, until, about eighteen months after commencing the experiment, the atmosphere in the bottles was perfectly colourless. One sample had passed into a viscid mass, exhibiting the usual characters; another, though it contracted to about one-tenth of its original volume, still retained to some extent its original appearance; crystals of oxalic acid were dispersed through the mass.

Corresponding experiments were made with the employment of nitrous acid in place of nitric peroxide, and the former was found to be much less rapid in its destructive action than nitrous acid; but gun-cotton when confined together with either of them, undergoes gradual decomposition even in the dark.

A sample of gun-cotton which had been found to decompose very readily at 100°, was placed in a retort suitably fitted with a delivery-tube, and the gases disengaged from it were passed into four bottles containing different samples of gun-cotton. These were then perfectly closed and exposed to strong daylight.

The first sample soon began to exhibit signs of change. The colour of the vapours increased in depth, and in one month's time had become very deep-coloured, the gun-cotton having assumed a greenish tinge from absorption of gas. The sample was then placed in the dark, after which it underwent further change very gradually, first contracting considerably, and afterwards, after the lapse of upwards of one year, becoming converted into a somewhat hard gum-like mass.

In the case of the second and third samples, the coloured vapours disappeared at first almost entirely, but the atmosphere in the bottles became coloured again after one month's exposure to light. The depth of colour increased so rapidly in one instance that two months after first exposure to light the bottle

was placed in the dark. The change in the two bottles then proceeded at about the same rate. The specimens contracted very slowly, and the nitrous vapours disappeared gradually. At present, two and a half years after commencement of the experiment, the specimen which has been exposed to light is scarcely as much changed as the one which after a time was placed in the dark; both have contracted to about one-half their original volumes, but have preserved their normal appearance; a few very minute crystals (probably oxalic acid) are perceptible upon the sides of the bottle which has been kept in the dark.

The fourth sample (prepared at Waltham Abbey in 1863) has resisted change to a remarkable extent. The vapours were at first entirely absorbed, and the gun-cotton has become slightly bleached. A faint orange tinge was first observable in the bottle after it had been exposed to strong daylight for six months. Nitrous vapours were then slowly evolved until the depth of colour was somewhat considerable. After the lapse of several months they gradually diminished again, and ultimately disappeared once more, after about eighteen months' exposure. After the lapse of two years and a quarter, the gun-cotton has contracted only slightly, but exhibits no other signs of change. There can be no doubt, however, judging from this contraction and from the evolution of vapours at one period of exposure, that this sample has suffered change which would not have occurred had it been exposed to light under ordinary conditions.

The experiments in sealed tubes, which have been described—the results of examination of gases collected from gun-cotton which has been exposed to heat for long periods in contact with them—and the general existence of nitric acid in samples of decomposed gun-cotton, appear to show that the first effect of exposure of the ordinary material to sufficient heat is the disengagement of nitric peroxide and the production of water, by which the former is converted into the nitric and nitrous acids; the latter, if allowed to remain in contact with the heated gun-cotton, is gradually reduced to nitric oxide, and finally the nitrogen becomes deoxidized at the expense of hydrogen and carbon, oxalic and carbonic acids being eventually furnished by the latter. The nitric acid produced attacks the gun-cotton at the same time; the presence of very small quantities of this

substance in gun-cotton greatly accelerates the decomposition of the material by heat. Thus one drop of concentrated nitric acid introduced into vessels containing 2 or 3 grms. of gun-cotton, invariably brought about rapid decomposition at comparatively low temperatures (55° to 65°); and by operating at temperatures between 70° and 100° with samples of gun-cotton to which as small a quantity as possible of dilute nitric acid was added, they were in this way generally converted into the gum-like product, in a few hours, though instances occurred occasionally in which, even under these severe conditions, the material resisted decomposition to a remarkable extent.

In many experiments instituted with ordinary gun-cotton at 90° and 100° it was found that, if the mode of operating were such as to facilitate the escape from the apparatus of any acid vapours evolved, the gun-cotton would frequently resist decomposition in a remarkable manner, being only very gradually converted into the final products; the two following experiments demonstrate how greatly decomposition at 100° C. can be retarded by impeding the destructive action of acid generated by the exposure to a high temperature.

In illustration of this, reference may be made to experiments in which equal quantities of the same description of gun-cotton were exposed, in suitable apparatus, for long periods to slow and rapid currents of heated air. In one week, the specimen exposed to a slow current had lost 49·9 p. c. in weight, while that which was exposed to a rapid current had only lost 8·92 per cent.

The experiments instituted leave no doubt that as soon as acid becomes liberated in gun-cotton, changes are developed in the material which would not be brought about by its simple exposure to heat, provided no free acid were present in it. If therefore it be possible to neutralize, at the instant of its liberation, any acid which may be produced by the effect of elevated temperatures upon the comparatively unstable impurities contained, in small quantities, in gun-cotton, the latter might be expected to resist alteration under circumstances which, if the first acidity were not counteracted, must determine the decomposition of the material.

Reference has been made in this paper, on more than one occasion, to the influence which certain mineral impurities of

general occurrence in gun-cotton (earthy carbonates) were observed to exert upon the rapidity with which the substance sustained alteration, upon exposure to heat. Some samples, which were heated for comparatively considerable periods without exhibiting signs of change, were found to contain much larger proportions of calcic and magnesian carbonates than specimens with which, in other respects, they were identical.

This observation led, at an early stage of these investigations, to a careful examination of the comparative effects of high temperatures (100° and 90° C.) upon a variety of samples, which were known to vary as regards the proportions of earthy and alkaline carbonates distributed through them. Some specimens were repeatedly rinsed in distilled water (whereby the larger proportion of earthy carbonates attached to the fibre was removed) and exposed to heat in comparison with corresponding specimens not thus treated. Other samples were extracted with dilute acid and washed; but as acetic acid was used in most of those experiments, the results of their exposure to heat were not of the nature anticipated, for the reason, as already explained, that the treatment in question removed, not merely carbonates, but also a proportion of the organic impurities. The extraction of the gun-cotton with dilute hydrochloric acid does not remove organic impurities; and, as has already been shown, this treatment has the effect of rendering ordinary gun-cotton more susceptible to the destructive effects of high temperatures.

A considerable quantity of Waltham Abbey gun-cotton, after having been purified in the usual way, was saturated with a solution of sodic carbonate of sufficient strength to deposit from 0·4 to 0·5 per cent. of the salt in the gun-cotton, after the latter had been expressed in the hydro-extractor and dried. Portions of the material thus prepared were carefully washed out in distilled water and submitted to heat in comparison with corresponding samples of the "alkalized" gun-cotton. The washing process did not merely extract the sodic carbonate, it also effected the mechanical removal of a large proportion of the earthy carbonates deposited upon the gun-cotton during the long-continued washing in spring- or river-water.

A large number of comparative experiments, at 100° and 90° C., were instituted with samples of gun-cotton which had been submitted to the various kinds of treatment just pointed

out. The following are some of the principal results observed.*

In experiments instituted at 100° C., with very considerable quantities of the "alkalized" gun-cotton, seven and eight hours elapsed before any symptom of decomposition was observed, while in operating with similar quantities of ordinary gun-cotton, decomposition became manifest in two hours and four hours. It was also observed that, when once the latter began to undergo considerable change, the decomposition proceeded much more rapidly in it than in the alkalized gun-cotton.

The influence of the small proportion of alkaline carbonate in retarding the decomposition of the gun-cotton was still more evident when smaller quantities of the material were operated upon. Thus, in one experiment the "alkalized" gun-cotton (containing 0·4 per cent. of sodic carbonate) exhibited the first indications of change in seven hours. and the ordinary gun-cotton in three hours after first exposure. The temperature of the latter afterwards rose much more rapidly and considerably, and the loss of weight sustained by it in three days' exposure was nearly double that which the "alkalized" sample suffered in four days' treatment, the alteration sustained by the latter specimen being comparatively slight.

In another experiment the "alkalized" sample exhibited no signs of change until after the lapse of seven hours, while equal quantities of the same sample, purified from carbonates by washing, exploded after exposure to 100° for 1·25 hour. Several similar results were obtained, and it was also clearly proved that the small proportion of earthy carbonates ordinarily existing in gun-cotton exert a decided protective action upon the material.

In the experiments instituted at 90° C., important proof of the protective effect of small quantities of carbonates was also obtained. Thus, some "alkalized" samples scarcely sustained any alteration by exposure for thirty-two to thirty-six hours to 90° C. during six days, while the same specimens of gun-cotton in the normal condition were considerably altered by similar treatment.

The "silicating" process prescribed by Von Lenk was found

* For details of experiments, *vide* Phil. Trans., part I, 1867, pp. 223–226.

to exert some amount of protective influence upon gun-cotton when exposed to heat; this result is, however, not due, as supposed by him, to the closing up of the fibre by an insoluble silicate, but simply to the deposition of a small quantity of earthy (and possibly of alkaline) carbonate upon the fibre when the silicate undergoes decomposition during the drying and the subsequent washing process. The amount of protection thus afforded to the gun-cotton is obviously as liable to variation as that resulting from the deposition of calcic and magnesian carbonates upon the material during the long-continued immersion in flowing water. Numerous specimens of gun-cotton which had been silicated, varied greatly in their powers of resisting change at high temperatures, but they were invariably rendered decidedly more prone to change if thoroughly washed in distilled water before exposure to heat.

It is remarkable how very small a proportion of a carbonate deposited upon the fibre of gun-cotton, exerts a notable influence upon its power of resisting the effects of heat. Thus, a portion of a sample of gun-cotton which had been carefully freed from carbonates, was saturated with perfectly clear lime-water, wrung out and dried. Upon exposure to 100° in comparison with an equal weight of the sample purified from carbonates, the very small quantity of calcic carbonate which had been deposited upon the gun-cotton proved sufficient to delay to a notable extent the period of first decomposition, and to modify somewhat the results of change produced by exposure for a definite period at 100° C.

In one of the experiments conducted at 90° C., the alkalized gun-cotton was heated in a flask to which a delivery-tube was attached, and the gas which escaped was examined. It was then observed that, upon the second day's exposure, a very small quantity of carbonic acid was continuously evolved; that the quantity increased somewhat upon the third day; and that no nitrous vapours escaped until the sixth day, when the temperature was accidentally raised to 95°. Carbonic acid was then still evolved in small quantity. Similar evidence of the slow decomposition of the carbonate, which always preceded any disengagement of nitrous acid, was obtained in other experiments.

Some gun-cotton, containing considerably larger proportions

of sodic carbonate than the samples previously employed, was prepared for experiment, with the view of obtaining data regarding the progressive effects of protracted exposure of "alkalized" gun-cotton to heat. The results obtained are fairly represented by the following selected experiments:—

6·5 grms. of Waltham Abbey gun-cotton were impregnated with 0·45 grm. of sodic carbonate. The air-dry specimen was exposed to 100° (for five or six hours daily), being loosely packed in a narrow-necked flask. Small weighed quantities of the sample (from 0·07 to 0·1 grm.) were removed from the flask for examination each morning before heat was again applied. The darkening, always produced by heating gun-cotton with an alkalized substance, commenced upon the first day's exposure to heat, but no other effect was noticed; after six days' exposure the gun-cotton was still slightly alkaline, the coloration having gradually increased, until some parts exhibited a brown tint. In other respects the substance was unchanged. After the ninth day's heating the gun-cotton was found to be quite neutral. About one-fifth of the specimen was then removed for examination. Water extracted the colouring-matter entirely, and a brown solution was obtained, in which sodic nitrate and nitrite were readily detected. The liquid also reduced cupric salts slightly. The gun-cotton itself had not suffered any change in explosiveness or strength of fibre, nor had the solubility in ether and alcohol increased appreciably.

The exposure of the sample to 100° C. was continued for seven days longer. On the sixth day a small portion was examined and found still to be neutral. On the seventh day, the atmosphere in the flask was found to have an acid reaction, though no nitrous vapours were perceptible.

Upon determining the weight of the gun-cotton (with deduction of the portions used during the experiment), it was found by calculation that the loss which it had sustained during exposure to heat for 100 hours (in sixteen days) was greater than would have been caused by the complete expulsion of carbonic acid from the carbonate employed. The aqueous extract was highly coloured, the gun-cotton being left almost colourless. Sodic nitrate and nitrite existed plentifully in the liquid, and the latter reduced cupric oxide in an alkaline solution. The washed gun-cotton was found, as might have been

anticipated, to have sustained a greater loss than would have been caused by the extraction of the alkaline base entirely in the form of nitrate. The gun-cotton soluble in ether and alcohol, now contained in the specimen, amounted to 6·98 per cent.; the material originally contained 2·3 per cent.; the increase amounted, therefore, only to 4·68 per cent. The proportion of nitrogen-oxides which would have been liberated by the reduction to that extent of trinitrocellulose, even to the lowest of the substitution-products, would not have sufficed to decompose the sodic carbonate present. It would appear from these results that the principal effect of the very long-continued exposure of this "alkalized" gun-cotton was to establish a very gradual action of the alkaline carbonate upon the gun-cotton (resulting in the production of glucic acid, &c.), and that even the *first* stage of decomposition (consisting in the production of soluble gun-cotton) caused simply by the action of heat upon the ordinary material, only proceeded to a very slight extent during the sixteen days' treatment.

In a second similar experiment, the exposure of the "alkalized" gun-cotton to 100° was continued until it was neutral. The sample was then extracted with water, and the proportion of nitrogen-acids existing in it as sodium-salts was determined by means of nascent hydrogen. The result showed that less than four-tenths of the sodic carbonate employed had been neutralized by those acids, the remainder existing in combination with organic acids. Traces of ammonia were evolved during the treatment of the gun-cotton in this and the preceding experiment, and the loss in weight sustained by the material was greater than would have been occasioned by the simple expulsion of carbonic acid from the carbonate. The solubility in ether and alcohol of the sample had only increased to about double the original proportion.

It was of course impossible actually to demonstrate by experiment whether the small proportion of organic acid produced in these experiments, which exhibited the property of reducing cupric oxide in an alkaline solution, was glucic acid, resulting from the action of the alkali upon the gun-cotton, or whether it consisted of the pectic acids found in the products of spontaneous decomposition; but as abundant proof exists that the latter are only the products of a *secondary* change resulting from the action upon gun-cotton of liberated nitrogen-acids,

there appear to be very good grounds for the conclusion that the results observed in these experiments were mainly ascribable to the action of the alkaline carbonate upon the gun-cotton and the organic impurities present, the effects which were exclusively due to the protracted exposure of the substance to 100° being limited to the liberation of a very small proportion of nitrogen-acid, which was at once neutralized. The only change produced in the gun-cotton by the action of heat consisted, therefore, in the decomposition of the small quantities of comparatively unstable organic impurities, and in a slight increase of the proportion of soluble gun-cotton.

The power possessed by carbonates to prevent or arrest the decomposition of gun-cotton when exposed to high temperatures, has been demonstrated in a striking manner by some experiments which have, at the same time, furnished evidence in support of the conclusion that the organic impurities contained in gun-cotton constitute the primary cause of its susceptibility to change under the influence of heat and light.

Specimens of gun-cotton were exposed in flasks to 90° and 100° until decomposition was established to such an extent that the vessels were filled with deep-coloured vapours; a small quantity of calcic or magnesian carbonate was then introduced into the flask, or the gun-cotton was removed from the vessel, dusted over with a carbonate, and immediately replaced. Decomposition was at once arrested by these means; moreover, the gun-cotton no longer exhibited any susceptibility of decomposition even if exposed to 90° and 100° for several successive days.

Some ordinary gun-cotton was dusted over with finely pulverized potassic bicarbonate* and exposed to about 95° in a long-necked flask, side by side with a corresponding quantity of the same specimen of gun-cotton in its ordinary condition. The "alkalized" gun-cotton gradually darkened upon the second day's exposure, eventually assuming a brown colour. After exposure to the above temperature during five days for seven hours daily, the unprepared gun-cotton began to evolve nitrous vapours abundantly. The examination of a small specimen

* The object of employing this salt was to exclude any protective effect which might be exerted in the course of the experiment by the absorption of moisture, if a calcic, magnesian, or sodic carbonate were employed, and a small quantity of the corresponding nitrate were produced.

showed that the sample had undergone very little change, the solubility in ether and alcohol having slightly increased.

It was now removed from the flask, dusted over with the powdered carbonate, and immediately re-exposed to heat. All decomposition ceased, the gun-cotton behaving exactly like the specimen which was originally alkalized, except that the usual darkening took place very slowly indeed. When it had been maintained at 95°—100°, seven hours daily for eight days, it was still alkaline; after treatment with water, it exhibited all the original properties of the gun-cotton; the solubility in ether and alcohol had undergone no increase since the alkaline salt was applied.*

The other specimen, to which the carbonate had been applied in the first instance, was examined after exposure to 95° for seven days. The aqueous extract had a brownish colour, and reduced cupric salt to a very slight extent. The extracted gun-cotton was perfectly white; the strength of fibre, explosiveness, and solubility in ether and alcohol had undergone no change. It was now dried and again exposed in a clean flask to 95°—100°. During six days it has not exhibited the slightest indication of decomposition; no acidity has yet been developed in it, and it is still unchanged in all its properties.†

It would appear from these experiments that a carbonate applied in the most simple manner to gun-cotton in which decomposition has been established, will effectually arrest the change; and that if gun-cotton containing a carbonate be exposed for some time to heat, the latter promotes the transformation of the unstable organic impurities into products fixed by the base, the result being that the gun-cotton undergoes a searching purification from these substances, and afterwards exhibits, in consequence, remarkable stability under very severe conditions of exposure to heat.

A number of experiments have been instituted on the comparative effects of exposure to 90° and 60° C. of samples of gun-cotton impregnated with different proportions of alkaline

* The exposure of this sample to 100° was afterwards continued for three weeks without any effect.—*June*, 1867.

† The exposure of this sample to 100° was continued for a total period of thirty days, after extraction of the carbonate, without any change resulting. A portion of the specimen was then exposed, seven hours daily for three days, to 115°, and it did not exhibit any symptom of change until the close of the third day.—*June*, 1867.

carbonates ranging from 1 to 10 per cent., the object being to ascertain whether the first-named proportion would suffice to afford security against the development of free acid in the gun-cotton, even under conditions of exposure to heat much more severe than could ever be met with in actual practice, or to determine what proportion might be necessary for that purpose. The results of these experiments showed that the presence of somewhat considerable proportions of alkaline carbonate (even as much as 10 per cent.) in gun-cotton does not exert any important action which can be pronounced prejudicial even under very severe conditions of exposure to heat, and that a proportion as low as 1 per cent. suffices to protect the material, for a longer period than ever could occur in actual practice, from the destructive action of such acid as may be liberated by the decomposition of the organic impurities or by the very gradual effect of high temperatures (90°—100°) upon the pure gun-cotton. It has also been abundantly demonstrated by the experiments detailed and by one instituted upon a more considerable scale, to be presently described, that even the introduction of one-half that proportion of sodic carbonate* into gun-cotton serves to afford it sufficient protection under conditions of exposure to heat exceeding in severity and duration any which the material would have to encounter if substituted for gunpowder in all directions.

III. *Protective Action of Water.*—In one of the earliest experiments on the effects of exposure of gun-cotton to 100°, it was found that the accidental introduction of a very small quantity of water into the vessel containing the gun-cotton, afforded most perfect protection to the material, which exhibited no signs of change during 16 hours' exposure to 100°, and had not sustained any loss in weight at the close of the experiment. This power possessed by water (or aqueous vapour) of preserving gun-cotton from decomposition at high temperatures is remarkably at variance with the influence exerted by moisture, if confined together with gun-cotton under protracted exposure to bright daylight and sunlight, in which case there appears no

* It is scarcely necessary to observe that this carbonate is selected for introduction into the gun-cotton because, while its solubility affords the means of its uniform distribution through a mass of material, it possesses no tendency to increase the hygroscopic properties of the latter.

doubt, from the results which have been described, that the aqueous vapour operates in determining to a slight extent the decomposition of the material.

Further illustrations, though less striking than the one above referred to, were furnished of the protective effect of aqueous vapour, by the comparative tardiness with which certain samples of gun-cotton, containing more than the ordinary proportion of hygroscopic moisture, underwent change by exposure to high temperatures. This preservative power of water has received the fullest demonstration from the results of a considerable number of experiments, the nature of which is fairly represented by the following examples.

1. A hank of gun-cotton was suspended in the upper part of a capacious flask containing distilled water tinted with litmus. The water was maintained in rapid ebullition for several hours, the greater portion of the steam condensed in the neck of the flask and upon the gun-cotton, returning to the body of water. At the conclusion of the experiment the tint of the litmus (compared with a standard) had not been affected in the slightest degree, and the gun-cotton was perfectly neutral and unaltered.

2. A rapid current of steam was passed over another specimen of gun-cotton uninterruptedly, seven hours daily, for three days, and not the slightest indication of development of acid or other change was obtained.

3. Gun-cotton was enclosed in sealed tubes, together with water, and exposed to 100° seven hours daily, for six days, without undergoing any alteration.

4. Some gun-cotton was thoroughly damped with water, and exposed in a sealed tube to 100° seven hours daily for twenty-four days. When the tube was opened, no gas issued from it; the gun-cotton exhibited a very faint acid reaction, but no other signs of change. After subsequent exposure to strong daylight and sunlight for six months, some slight indications of change were obtained, but the strength of fibre of the specimen was unaltered, and there was no appreciable diminution in its explosiveness.

5. Seven grms. of gun-cotton were thoroughly moistened, and then placed in a flask, which was connected by a delivery-tube with another containing water, and was also fitted with a straight narrow glass tube. A small quantity of steam was passed into the flask from time to time, as the moisture became partially

expelled during the experiment. After three days' exposure to 100° (six hours daily), a weighed sample was removed for examination. The gun-cotton had become slightly discoloured in a few places, where it was in immediate contact with the sides of the flask. Water extracted a minute quantity of colouring-matter; no other effect of the exposure to heat was observed. The gun-cotton was again heated to 100° for five days, six hours daily; it was then removed, dried and weighed. By these eight days' exposure to 100° in a moist atmosphere, it had sustained a loss of only 1·7 per cent. A weighed portion was again examined; it furnished a very faint indication of acidity. The reactions of nitric acid could not be obtained with the aqueous extract; the proportion of matter extractable by ether and alcohol had very slightly increased.

The sample was again moistened, and exposed to 100°, as before, for nine days; at the expiration of this period it had sustained a further loss of 1·01 per cent. The total loss during the seventeen days' treatment amounted therefore to 2·71 per cent. The condition of the sample was now as follows:—it had darkened in a few places where it was in close contact with the glass, and possessed a faint odour, such as is always observed in gun-cotton which has been stored for some time in a warm locality; its acidity had not increased, but a faint reaction of nitric acid was obtained in the aqueous extract after concentration to a small bulk. A trace of lime was also found in solution (evidently as calcic nitrate produced from carbonate in the sample). The proportion of matter extracted by ether and alcohol amounted to 4·1 per cent.; in its original condition the sample contained 2·3 per cent.

6. Other samples of gun-cotton were saturated with moisture, and exposed to 100° in vessels which afforded facilities for the very gradual escape of the water. The exposure to heat was continued until no signs of moisture were perceptible in the cool portions of the apparatus. Nitrous vapours then soon made their appearance; upon examining the gun-cotton, it was found to contain a very small quantity of nitric acid, and had become almost perfectly soluble in ether and alcohol; the insoluble portion amounting in one instance only to 1·25 per cent.

It appears from these experiments that gun-cotton, if confined in an atmosphere saturated with aqueous vapour,

resists decomposition when exposed for long-continued periods to 100° C.; and that if the aqueous vapour which protects the gun-cotton is allowed to escape slowly during the exposure to 100° until that substance and the atmosphere surrounding it have become almost dry, decomposition sets in very gradually; so that by arresting the change at a particular period the material is found to be completely reduced to soluble gun-cotton, without the formation of any appreciable amount of the secondary products which result from the action of liberated acid upon the cellulose products.

The perfect protection afforded by moisture to gun-cotton at 100° C., under severe conditions, rendered any experiments in this direction at somewhat lower temperatures almost unnecessary. Very important confirmatory evidence of the protective action of moisture has, however, been furnished by some experiments continued for many months with comparatively large quantities of gun-cotton at temperatures ranging from 60° to 65° C.*

Careful observations have been instituted upon the storage of considerable quantities of the material in a wet or merely moist condition. Ordinary gun-cotton has been immersed in sufficient distilled water just to cover it, and has been kept in that condition in closed vessels, with light excluded, for two and a half years. It is perhaps scarcely necessary to state that the material has not sustained the slightest change, and that the distilled water in which it has been preserved is perfectly neutral, the only impurity found in the latter being a small quantity of saline matter extracted from the gun-cotton. A portion of this sample was transferred to a large glass bottle twelve months ago, and has been left exposed to diffused daylight. This difference in the mode of preservation has been quite without effect upon the gun-cotton.

The principal stock of gun-cotton manufactured at Waltham Abbey for experimental purposes, amounting to about 3,000 lbs., has been preserved in a moist condition (just as obtained from the centrifugal hydro-extractor) in closed cases until required for use, some of the packages having been kept for about two years; a few, specially set apart for periodical examination, have been preserved for about three years. I have to record no indications of the slightest change except in instances where

* Phil. Trans., part I, 1867, p. 236.

the gun-cotton had been preserved in close contact with the tinned-copper linings of some gunpowder cases used for its storage. It was found, after some time, that the surfaces of these became oxidised where they were in contact with the moist material, and that this oxidation determined the development of an acid reaction in the gun-cotton, which, however, was, and has continued to be, confined to the portions in immediate contact with the surface of metal.*

Gun-cotton in the condition above referred to contains sufficient water to render it quite uninflammable; it may therefore be preserved with perfect safety in this convenient condition, and may be at any time prepared for use by desiccation. As far as can be concluded from three years' experience, the close packing of gun-cotton in this damp state is not, even in the slightest degree injurious to the structure of the fibre, no tendency whatever of the material to become rotten when thus preserved having yet been discovered. On the contrary, most decided evidence has been obtained that gun-cotton, when kept in a damp condition, is very considerably more permanent than ordinary cotton, or vegetable substances of similar nature.†

PART IV.—OTHER OBSERVATIONS, INSTITUTED UPON LARGE QUANTITIES OF GUN-COTTON.

A series of observations has been conducted for about three years under my direction and in accordance with a programme approved of by the Committee on Gun-cotton, for the purpose of ascertaining the effects of storage in considerable quantities, under the ordinary atmospheric conditions of this country, and under conditions, as regards temperature, representing the extremes likely to be met with in tropical climates or in warm localities (*e.g.*, the magazines of ships). The gun-cotton, which,

* The readily oxidizable character of tin and the tendency of a metal to establish, by its own oxidation, that of readily oxidizable substances which are in contact with it, are well known. If gunpowder containing even the ordinary proportion of moisture remain in contact with a surface of tin, the metal becomes oxidized and the gunpowder acquires an acid reaction, sulphuric acid being detected after some time. Similarly, some remarkable instances of the oxidation of iron by contact with somewhat damp gunpowder, attended by the production of sulphuric acid, have come under my notice.

† Phil. Trans., part I, 1867, p. 238.

with these objects in view, was closely packed in large ammunition-boxes, comprised not simply parcels of the material as obtained by following the present system of manufacture, but also others in the production of which modifications had purposely been introduced with the view of determining the influence which might be exerted, by possible accidental departure from one or other of the fixed regulations of manufacture, upon the stability of the material. The following is a summary of the observations made up to the present time.

I. *Storage of Gun-cotton under ordinary conditions of Temperature.*

(a.) *The Gun-cotton being closely packed in a damp condition.*—Attempts have been made to ascertain whether the close packing of gun-cotton in a damp condition would render it liable to spontaneous heating. Comparative experiments were instituted with gun-cotton, and with cotton-wool in its original unpurified condition. The materials were prepared in two ways; in one experiment they were exposed to an atmosphere saturated with moisture until about 5 or 6 per cent. of water had been absorbed; they were then closely packed in boxes; in another a small portion was moistened (the excess of water being expressed) and packed in the centre of a considerable quantity of dry material. These packages were first occasionally exposed to the sun, they were afterwards preserved for several weeks in a chamber, the atmosphere of which was artificially heated; but in neither instance could any indication of the development of heat be obtained, although the external temperature frequently reached and sometimes exceeded 50°. The inference drawn from these negative results is that gun-cotton is not more liable to spontaneous heating than ordinary cotton-wool. The latter was exposed in a damp and very closely packed condition, in quantities of from ten to thirty pounds, to a heated atmosphere for several months, in order, if possible, to establish spontaneous heating under conditions to which gun-cotton might afterwards be submitted, but the experiments were without result.

(b.) *The Gun-cotton being closely packed in an ordinarily dry condition.*—Large ammunition-boxes were closely packed with gun-cotton of the following kinds:—

(1.) Prepared strictly in accordance with the directions laid down by Von Lenk (*i.e.*, including the "silicating" treatment).

(2.) The same, made up into cartridges.

(3.) Prepared in the ordinary manner, but not "silicated."

(4.) Not "silicated," and packed together with a few skeins (1¼ lb.) of gun-cotton which had only been purified by washing in water (the treatment with alkaline water having been omitted).

(5.) Not "silicated," and packed together with some gun-cotton soluble in ether and alcohol.

(6.) Ordinary gun-cotton impregnated with about 0·3 per cent. of sodic carbonate.

Pieces of litmus paper were placed in different parts of the various packages.

Cases containing Nos. 1, 3, and 6 were packed in July and September, 1864, and stored in a dry locality. During the summer months the maximum temperatures recorded in this store-room ranged from 16°·5 to 24°. About six months after the boxes were packed, one of each kind was opened for examination. All the samples had a faint, peculiar odour, like that of pine-wood, which is always developed in the closely-packed material, and was most marked in the unsilicated gun-cotton. Some parts of the litmus paper enclosed in the latter had assumed a pink tinge, and where it had been placed between the gun-cotton and the metal surface of the packing-case, it was decidedly reddened in spots; the tin surface, moreover, exhibited slight signs of oxidation in some places where it was in very close contact with the gun-cotton.* The litmus in the "silicated" and "alkalized" gun-cotton was unaffected, except again, in one or two small places where it had been interposed between the gun-cotton and the metal surfaces. The boxes were closed immediately after inspection and examined eight months afterwards, when they were found quite unaltered; the litmus paper in the centre of the unsilicated gun-cotton had not been at all affected, but, as before, it was slightly reddened where it had been in contact with the metal.

* A piece of bright sheet tin which was packed on this occasion in the centre of the gun-cotton was examined after a period of one year and found to have become corroded in spots, the gun-cotton having a slight acid reaction at the places where this effect was produced.

After further preservation for eighteen months, the boxes were again inspected; their condition was precisely what it was on the previous examination.

Storage in a closely-packed condition for nearly three years has, therefore, not at all affected the gun-cotton in these three states. The material which was not silicated has affected, to a slightly greater extent than the others, the metal surfaces with which it has been in close contact.

Some other cases containing portions of the stock of gun-cotton, "silicated" and not silicated, manufactured in the summer of 1863, and preserved since that time ($3\frac{3}{4}$ years) in a closely packed and ordinarily dry condition, have also been recently inspected, and their contents have been found to be as perfect as those of the cases just described.

The cartridges enclosed in serge bags were packed and stored about $2\frac{1}{4}$ years ago. Their condition is unaltered, and the metal cases containing them are perfectly bright.

The cases containing a proportion of imperfectly purified gun-cotton and of soluble gun-cotton (Nos. 1 and 5) were packed early in January, 1866. After storage for fifteen months their contents have been examined and found to present no points of difference from the other packages of gun-cotton above described, the only indications of acidity being discovered where the metal surfaces and the gun-cotton were in very close contact.

II. *Exposure of large packages of Gun-cotton, in different conditions, to Heat.*

(a) *Preliminary Experiment.*—A wooden box, holding $4\frac{1}{4}$ lbs. of gun-cotton when closely packed, was fitted with a gutta-percha tube intended to receive a thermometer. The sides of the tube were perforated in several places, and it passed horizontally through the centre of the box, the openings being closed with corks. The box was painted black, and, having been tightly filled with skeins of gun-cotton, was placed in the open air throughout each day in the month of August, 1864, in a position where it would be most frequently exposed to the sun's rays, and would also receive the heat radiated from a brick wall.*

* The box was removed indoors late in the afternoon, and replaced at nine in the morning. It was also placed under shelter when rain fell.

A registering thermometer was enclosed in the tube of the box, and another was placed on the outside, readings being taken of both twice daily. The highest temperature indicated upon the exterior of the box was generally about 6° or 7° above that of the centre of the gun-cotton. The temperature of the latter ranged from 14° (early in the morning) to 38°, while the temperature-indications on the exterior of the box ranged between 15° and 47°. The average temperature in the centre of the box at five o'clock in the afternoon was 32°. At the close of the month the box was opened; the gun-cotton possessed the faint odour peculiar to the material when closely packed, but exhibited no signs of change.

The box was immediately reclosed (some litmus paper being introduced) and placed in a chamber, where the temperature was artificially maintained, as constantly as possible, at 50°. During one month's exposure in this chamber the temperature of the centre of the box was stationary at about 49° for some time on four occasions; but the maximum temperature attained during the day ranged, with those exceptions, between 43° and 47°. At the expiration of the month, the litmus paper was found to be reddened, and the gun-cotton had a somewhat pungent odour. A portion of it furnished, with cold water, a very faintly acid liquid. No nitric acid could be detected, and, with the exception of the peculiar odour, the gun-cotton gave no indication of change. It was returned to the box together with litmus paper, and exposed again to heat in the chamber for a few days. The litmus had been changed as before. The gun-cotton was now removed from the box and fully exposed to air for an hour, when it was repacked, together with litmus paper, and placed in an apartment at the ordinary atmospheric temperature. The contents of the box were inspected weekly; a very trifling reaction was produced upon the litmus in some parts only, and this effect did not increase.

The gun-cotton was afterwards repacked, a very imperfectly purified skein being placed in the centre. It was then kept in the warm chamber as before for seven months. When the box was again opened, the litmus paper was red and rotten, and the material possessed a pungent odour, but no nitrous vapours were perceptible. One of the skeins in immediate contact with the imperfectly purified gun-cotton was extracted with water, but furnished only a very faintly acid liquid. The box was repacked

as quickly as possible, all apertures were perfectly closed up, and it was placed in a magazine. After the lapse of one year and three-quarters it was examined, and its contents were found unchanged, except that the odour was decidedly less pungent than before.

The data furnished by this preliminary experiment appeared to warrant the conclusion that further and more extensive trials of the effects of heat upon gun-cotton might be safely instituted. The following experiments were, therefore, made :—

b. *Exposure of a large case of Gun-cotton to the Sun's rays.*—A large wooden box with blackened exterior, and fitted with a central tube to receive the recording thermometer, was completely filled with rather more than 36 lbs. of gun-cotton, *not* silicated, which had been manufactured two years previously. This box was exposed to the open air on all bright sunny days between the middle of April and 1st of October last year; it was placed at a short distance from the brick-wall of a hot-air chamber, in a position where it would be exposed to the maximum available amount of sunlight. At night and during wet weather it was placed under shelter. Readings were taken every two hours of the thermometer in the central tube, and of one exposed upon the outside of the box. The extreme temperature attained by the centre of the gun-cotton was 35°, the thermometer upon the box having indicated 49° on that day. Upon several occasions the thermometer in the centre of the box recorded 32°·5. The latter generally attained its maximum temperature from four to six hours after the highest external temperature had been registered.

When the box was opened, the litmus paper was found to have assumed a pink tinge, and the usual faint odour of confined gun-cotton was somewhat more manifest than if the box had been preserved under ordinary atmospheric conditions, but the material itself was quite unchanged.

c. *Exposure of Gun-cotton in different conditions to a heated atmosphere in a confined space.*—A chamber was constructed of brickwork, and suitably fitted for the reception of a number of large ammunition-boxes. A system of iron pipes, standing in the centre of the chamber, was supplied with hot water from a boiler placed in a shed distinct from the chamber and heated with gas. By this arrangement, the atmosphere in the room

could be maintained at artificial temperatures without risk of accident.

The boxes in which the gun-cotton was packed were the large ammunition-cases employed in military service, and consisted of thin tinned-copper canisters enclosed in stout wooden boxes, and very tightly closed with double lids. Experience showed, some time after the experiment was set on foot, that the employment of these metal-lined cases was unquestionably prejudicial to the gun-cotton, as the very slightest development of acid in the latter, where it was in actual contact with the sides of the case, established oxidation of the metal surfaces, whereby in turn the alteration of the gun-cotton at those parts was considerably promoted. Each case was fitted with a central tube to receive a registering thermometer. The gun-cotton was closely packed, and the description of material placed in the several boxes was varied, with the view of examining the effects of different modifications in the manufacture upon the power of gun-cotton to resist the effects of heat.

In the first instance, the temperature of the hot-air chamber was raised as rapidly as possible to between 49° and 50°, and then maintained at that temperature (within narrow limits on either side) for several hours daily; periodical readings of a thermometer exposed in the room and of those enclosed in the central tubes of the boxes were recorded. The heating of the chamber was commenced at six in the morning; the maximum temperature was generally attained at about eleven o'clock, and it was maintained until six in the afternoon.

After the first day of the experiment the temperature of the air in the chamber at six in the morning was always from 8° to 11° lower than the temperatures recorded in the boxes, excepting on the Monday morning, when the difference amounted only to between 1° and 3°. The rapidity with which the temperature rose in the interior of the boxes varied somewhat; the thermometers were stationary, or fell slightly, for about two hours after the heating was commenced; at the close of that period the air in the chamber was generally (except on Mondays) 10° or 12° higher than that of the centre of the gun-cotton, the latter then rose gradually, almost reaching the maximum in ten hours, but still rising 2° or 3° in the last two hours. Even after seven hours' exposure to air at the maximum

temperature, the contents of the case were, in the centre, from 5° to 9° cooler than the external air. The daily records of temperature obtained from the different boxes during three months' exposure to a maximum temperature of 50° were very uniform, and not the slightest indication of any development of heat in the mass of the gun-cotton was obtained in any one instance. The maximum temperatures within the boxes were always considerably below the temperatures of the air in the chamber at the time, the difference ranging between 6° and 11°, excepting on Mondays.

At the termination of three months the temperature of the chamber was raised to between 54° and 55°, and readings of the thermometers were taken every two hours. The temperature of the chamber was generally raised to 54° by about eleven in the morning, and was maintained as constantly as possible at that temperature for seven hours. On 79 days out of 195, the temperature of the room reached 55°·5, and continued so from two to four hours. During three months no indication of development of heat was obtained in any one of the boxes; the temperature-records within these at the close of the day were during this period (excluding Mondays) from 6° to 11° below that in the chamber itself, and the highest maximum temperature attained by the boxes up to the termination of that period was 49°. One of the boxes then furnished indications of some development of heat in its contents; it was, therefore, removed, and the experiment was continued with the remainder of the boxes. During the last three months the maximum temperatures recorded in the several boxes confined in the chamber, more nearly approached that of the air surrounding them; the differences between the readings of thermometers within and outside the boxes at six in the evening ranged between 5°·5 and 1°.

The results furnished by these experiments* were as follows:—

(1.) Gun-cotton closely packed in metal-lined cases, of considerable size, in two of which some imperfectly prepared gun-cotton was purposely included, sustained a daily exposure for twelve hours during three months to a heated atmosphere, the temperature of which generally ranged from 49° to 51° for a

* For details of the experiments, *vide* Phil. Trans., part I, 1867, p. 245.

period of seven hours, without furnishing any indication of the development of heat, consequent upon chemical change.

(2.) The further exposure of these packages for another period of three months to a heated atmosphere, the temperature of which generally ranged during seven hours daily between 54° and 55°, resulted only in *one* instance in the development of heat in the gun-cotton; and the particular box which, at the expiration of the six months' treatment, furnished this indication that its contents were undergoing decomposition, was filled with gun-cotton in the condition which all previous experiments had indicated as least capable of resisting the effects of prolonged exposure to heat; being, namely, almost free from substances (carbonates) which would exert a neutralizing action upon any acid generated by decomposition of the comparatively unstable impurities existing in the gun-cotton.

(3.) The box which next furnished very slight indications of the development of heat, after exposure for 6¼ months, contained gun-cotton through which a small proportion of earthy carbonates had been distributed by its submission to the so-called "silicating process," but in the centre of which a specimen of imperfectly purified gun-cotton had been packed. There is no question that this box would have furnished much earlier indications of the occurrence of chemical change in its contents, if the gun-cotton principally composing the latter had not been protected for a considerable period, by the presence of carbonates, from the destructive effects of acid liberated from the imperfectly purified gun-cotton which was packed in the centre of the box.

(4.) A box of "silicated" gun-cotton containing a small quantity of soluble gun-cotton not silicated, was the next to exhibit symptoms of decomposition, after having been exposed to heat for seven months. It has been shown that the soluble gun-cotton is not more prone to decomposition than the most perfectly converted material; but the sample packed in the centre of this box was not protected by carbonates, and therefore doubtless sustained change considerably sooner than the chief portion of the contents of this box, promoting an alteration in the latter after the lapse of some time, when the protective effect of the carbonate had become neutralised.

(5.) The box which was entirely filled with gun-cotton, prepared strictly according to Von Lenk's system, including its

submission to the "silicating" process, only exhibited a slight indication of internal development of heat after having been exposed for *eight* months to a heated atmosphere. The protective effect exerted by the small proportion of earthy carbonate deposited in the gun-cotton as a result of the "silicating" treatment was, in this instance, not diminished by the presence of any gun-cotton not thus treated, and consequently the contents of this box resisted change for a longer period than the "silicated" gun-cotton in two other boxes (2 and 3). Moreover, this gun-cotton, though exposed to heat for two months longer than the unsilicated gun-cotton, was found upon examination to have evolved considerably less acid.

(6.) The gun-cotton which had been uniformly impregnated with only 0·3 per cent. of sodic carbonate furnished no signs whatever of development of heat up to the period when the experiment was interrupted, having been at that time exposed for ten months to a heated atmosphere, the temperature of which ranged, for seven hours daily during seven months, between 54° and 55°. It is much to be regretted that a careful examination of the contents of this box after so prolonged and severe an exposure to heat was prevented by an accident.

(7.) The condition of the gun-cotton after exposure to heat in the three boxes first removed was very similar. Although the material was found to be highly impregnated with nitric oxide and nitrous acid (the development of which there is every reason to believe had been very considerably promoted by the large metal surfaces of the boxes which were in close contact with the gun-cotton), the decomposition had not proceeded in any one of the boxes to such an extent as to produce an alteration in the explosive and other properties of the gun-cotton. When the latter had been purified from the free acid developed in it, no difference could be discovered between it and the original material, except that it had become slightly bleached. The gun-cotton from boxes 1 and 2, after being purified by digestion in alkaline water and subsequent repeated washing in distilled water, was dried, repacked and returned to the hot-air chamber. It now contained no carbonates whatever by which the destructive effect of acid, if developed, could be retarded or prevented; but the boxes, each containing 11 lbs. of this gun-cotton, were exposed to heat for three months, the temperature of the air ranging from 54° to 55°·5 for seven hours

daily, and no indication whatever of development of heat was obtained in either instance. (The purified gun-cotton from boxes 3 and 4 was also repacked and returned to the chamber at later periods.)

After the heat-experiments described above had been continued between eight and nine months, two barrels, fitted with tubes for thermometers, each containing about 23 lbs. of gun-cotton, which was neither "silicated" nor impregnated with sodic carbonate, were placed in the chamber, the object being to obtain direct proof of the extent of influence exerted by the metal surfaces in the cases employed in the other experiments, upon the behaviour of the gun-cotton itself.

Two other much smaller metal-lined cases, each containing about 5 lbs. of gun-cotton, were also placed in the chamber at this time; one of them was filled with a sample which had already been subjected to severe exposure to heat, and had subsequently been purified from acid, and the other was filled with discs prepared by compressing gun-cotton which had been reduced to pulp. Lastly, an ammunition case containing 23 lbs. of gun-cotton, which was impregnated with a more considerable quantity of sodic carbonate than employed in the first experiment, was added to the contents of the chamber. The heating of the latter to 54°—55° was continued for about six weeks, when an explosion occurred which destroyed the chamber and the whole of the samples, excepting some of the compressed gun-cotton.

As is generally the case in accidents of this kind, the immediate cause of the explosion could not be traced with certainty. The usual periodical readings of the thermometers enclosed in the packages had been taken shortly before the explosion occurred, and all the temperatures last recorded were below that of the air in the chamber, which had been at 55°·5 from two till six o'clock; not one of the packages had furnished any indication that heat was developed, but the temperature in the two small boxes was considerably higher than in the larger packages; the comparatively small volume of gun-cotton became much more rapidly heated throughout, so that the temperature recorded in these instances at the close of the day's heating was generally within 2° of the maximum external temperature. It appears most probable, therefore, that the small parcel of gun-cotton which had already suffered some change by exposure to

heat, and which had since been exposed for six weeks to a heated atmosphere ranging between 54° and 55°·5 for seven hours daily, eventually sustained further alteration, which, though very gradual for a time, at length increased to such an extent that heat was very rapidly developed, raising the gun-cotton to the temperature required for its explosion within a comparatively brief period. The experiments made at 100° C., with small quantities of gun-cotton which have been described in an early part of this paper, demonstrated that, when once a considerable decomposition of the substance had set in, the development of heat was very rapid indeed. It was believed, however, that the *first* establishment of decomposition would in all instances be indicated by so gradual a rise of temperature that frequent periodical observations of a thermometer placed in the centre of packages of heated gun-cotton would always afford the means of carrying on experiments of this class with security, a belief which was strongly supported by the results of the experiments carried on for periods of five, six, and ten months with the five large packages of gun-cotton. The power to resist serious decomposition upon continued exposure to a highly heated atmosphere had proved so unexpectedly great in the case of every one of those experiments, that it was considered important to ascertain, if possible, the full extent of those powers; and hence, with what proved to be undue reliance upon the infallibility of the measures adopted to guard against accident, the experiments were protracted and the variety of the tests increased, far beyond the extreme limits necessary for the attainment of their original object, which was to ascertain how far gun-cotton, either of ordinary manufacture, or accidentally defective, or protected by special preparation, would resist change under conditions representing the extremes, both in extent and duration, of heat to which it might be exposed if stored, or used in active military service, in tropical climates.

The Committee on Gun-cotton has endeavoured to collect reliable data with reference to the average and extreme temperatures to which gun-cotton might be exposed in ships' magazines, during the passage of vessels through tropical regions, or to which it might be subject in India if directly exposed to the sun in ammunition-boxes; these being the most severe natural conditions of exposure to heat which would ever be likely to occur. A statement was furnished to General Sabine, by the late

Admiral FitzRoy, of the maximum and minimum temperatures recorded monthly in the chronometer-room of Her Majesty's Ship "Odin," between September, 1861, and September, 1863, this vessel having been during that period at Japan, in the China Sea, Malacca Strait, Indian Ocean, Bengal Bay, North and South Atlantic, &c. The highest temperatures recorded were in May, 1862, and April, 1863 (in the Indian Ocean), being 31° on both occasions; the minimum temperatures in those months were 29° and 26°·8. Between February, 1862, and August, 1863, the registered maximum temperatures ranged between 25°·3 and 31°, and the minimum temperatures between 14°·7 and 29°. Admiral FitzRoy considered that, except at times when men were continuously at work in a ship's magazine, the temperature within the latter would be regulated by that of the surrounding water, which, at a few feet below the surface, is never warmer than from 26° to 30°. If this is the case, the temperature-records obtained from the "Odin" afford a fair representation of the maximum and minimum temperatures of the atmosphere in magazines where gun-cotton might be stored on board ship.

At the request of General Sabine, Mr. Pogson, the Astronomer of Madras, took daily readings, from May 1 to June 30, 1866, of thermometers placed in boxes, the one painted black and the other white, and both exposed to the sun. That gentleman has reported, that during the above-named period, which occurred in the hottest and driest season ever experienced at Madras, the highest temperature registered inside the black box was 51°·2, that in the white box being 44°, whilst the lowest minimum readings recorded were 26°·8 in the black box, and 26°·1 C. in the white box.* The maximum temperature recorded *in the empty black box*, exposed to the sun at Madras, was therefore about 5° C. below the average temperature to which closely packed gun-cotton, in a condition most favourable to change, was exposed for about seven hours daily, during three months (having previously been similarly exposed in an atmosphere at 50° for an equal period), before there was any indication of development of heat, while gun-cotton prepared according to Von Lenk's directions resisted a similar exposure for five months, and ordinary gun-cotton containing a small proportion

* The difference between the maximum records in the black and white boxes is reported as ranging between 3° and 7°.

of sodic carbonate furnished no indication of change when it had been stored under the same circumstances for seven months.

General Morin*, in some observations upon the recent report of Pélouze and Maurey on gun-cotton, referred to the existence of instances in which the atmosphere in the interior of buildings had been raised to a temperature of 38°, 40°, or 42° (the external atmosphere being only 21°) by the passage of solar heat through glass windows or roofs, and also stated that it was not uncommon to find the interior of powder-wagons, covered with metal, at a temperature of 50°—60°, while the external temperature was only 24°. It is evident from the nature of this statement that the elevation of temperature to this extent in the localities described was only transient; but even if the atmosphere in magazines or ammunition-wagons were occasionally at such temperatures for several consecutive hours during a considerable period, it may be confidently maintained that gun-cotton properly purified and impregnated with a small proportion of sodic carbonate, may be preserved in such localities with perfect safety, even in a closely packed condition. It has been shown that gun-cotton, even without the aid of the very decided though variable protection afforded to it by the "silicating" process, sustained no change whatever by continuous exposure to the sun's rays in a black box between April and September, the temperature of the external surface of the box having frequently exceeded 40°, and that the same kind of gun-cotton sustained, without any change, three months' exposure for several hours to an atmosphere of 50°, and did not exhibit any indication of change until after further exposure for nearly three months to an atmosphere maintained for several hours daily at 54°·5—55°·5. In both these instances the gun-cotton was as closely packed as possible, in one mass.†

It is therefore considered that the extent and circumstances of exposure to heat which even this perfectly unprotected gun-cotton resisted, may be regarded as exceeding in severity such as it would have to encounter in the actual employment of the material in naval and military service.

* Comptes Rendus, vol. lix, p. 374.

† In ammunition-wagons, the gun-cotton would be packed in the form of cartridges, enclosed in serge, and with intervening air-spaces. It would therefore be in a condition much less favourable to the accumulation of heat, than the gun-cotton was, in the experimental cases.

The following are some of the principal conclusions which may be drawn from the results of observations and investigations described in the foregoing pages:—

1. Gun-cotton produced from properly purified cotton, according to the directions given by Von Lenk, may be exposed to diffused daylight, either in open air or in closed vessels, for very long periods without undergoing any change. The preservation of the material for $3\frac{1}{2}$ years under those conditions has been perfect.

2. Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in gun-cotton of the description defined above; the statements which have been published regarding the very rapid decomposition of gun-cotton when exposed to sunlight do not therefore apply to the nearly pure trinitrocellulose obtained by strictly following the system of manufacture now adopted.

3. If gun-cotton in closed vessels is left for protracted periods exposed to strong daylight and sunlight in a moist or damp condition, it is affected to a somewhat greater extent; but even under these circumstances the change produced in the gun-cotton by several months' exposure, is of a very trifling nature.

4. Gun-cotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed into boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary storehouses (as far as the experience of three and a half years has shown).

5. Gun-cotton prepared and purified according to the prescribed system, and stored in the ordinarily dry condition, does not furnish any indication of alteration, beyond the development, shortly after it is first packed, of a slight peculiar odour, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

6. The influence exercised upon the stability of gun-cotton of average quality by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates, is very trifling in comparison with the results recently published by continental experimenters relating to the effects of heat upon gun-cotton; *and it may be so perfectly counteracted* by very simple means, which in no way interfere with the essential

qualities of the material, that the storage and transport of gun-cotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident, than is the case with gunpowder.

7. Perfectly pure gun-cotton, or trinitrocellulose, resists to a remarkable extent the destructive effects of temperatures even approaching 100° C.; and the lower nitro-products of cellulose (soluble gun-cotton) are at any rate not more prone to alteration, when pure. The incomplete conversion of cotton into the most explosive product does, therefore, not of necessity result in the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid-mixture.

8. But all ordinary products of manufacture contain small proportions of organic nitrogenized impurities, of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matters retained by the cotton fibre, and which are not completely separated by the ordinary or even a more searching process of purification.

It is the presence of this class of impurity in gun-cotton which first gives rise to the development of free acid, when the substance is exposed to the action of heat; and it is the acid thus generated which eventually exerts a destructive action upon the cellulose-products, and thus establishes decomposition which heat materially accelerates. If the small quantity of acid developed from the impurity in question be neutralized as it becomes nascent, no injurious action upon the gun-cotton results, and the great promoting cause of the decomposition of gun-cotton by heat is removed. This result is readily attained by uniformly distributing through gun-cotton a small proportion of a carbonate, the sodic carbonate, applied in the form of solution, being best adapted to this purpose.

9. The introduction into the finished gun-cotton of one per cent. of sodic carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated temperatures as would induce some decomposition in the perfectly pure cellulose-products. That proportion affords, therefore, security against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to gun-cotton might exert upon its properties as an explosive, would consist in a

trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

10. Water acts as a most perfect protective to gun-cotton (except when it is exposed to sunlight), even under extremely severe conditions of exposure to heat. An atmosphere saturated with aqueous vapour suffices to protect it from change at elevated temperatures, and wet or damp gun-cotton may be exposed for long periods in confined spaces to 100° without sustaining any change.

Actual immersion in water is not necessary for the most perfect preservation of gun-cotton; the material, if only damp to the touch, sustains not the slightest change, even if closely packed in large quantities. The organic impurities, which doubtless give rise to the very slight development of acid observed when gun-cotton is closely packed in the dry condition, appear equally protected by the water; for damp and wet gun-cotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from wet gun-cotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient not only to act as a perfect protective, but also to guard against all risk of accident. It is therefore in this condition that all reserve stores of the substance should be preserved, or that it should be transported in large quantities. If the proper proportion of sodic carbonate be dissolved in the water with which the gun-cotton is originally saturated for the purpose of obtaining it in this non-explosive form, the material, whenever it is dried for conversion into cartridges, or employment in other ways, will contain the alkaline matter required for its safe storage and use in the dry condition in all climates.

Although some experiments bearing upon the different branches of inquiry included in this memoir are still in progress, with a view to the attainment of additional knowledge of the conditions which regulate the stability of gun-cotton, it is confidently believed that the results which have been described amply demonstrate that the objections which have been of late

revived, especially in France, against the employment of gun-cotton, on the ground of its instability, apply only in a comparatively slight degree to the material produced by strictly pursuing the system of manufacture perfected by Von Lenk; that, as far as they do exist, they have been definitely traced to certain difficulties in the manufacture of *pure* gun-cotton which further experimental research may overcome; but that, in the mean time, these objections are *entirely set aside* by the adoption of two very simple measures, against the employment of which no practical difficulties can be raised, and which there is every reason to believe must secure for this material the confidence of those who desire to avail themselves of the special advantages which it presents as an explosive agent.

NOTE.—Since this memoir was communicated to the Royal Society, a circumstance of a very unexpected nature has been observed, accidentally in the first instance, which appears to have an important bearing upon the question of the stability of gun-cotton.

A skein of Waltham Abbey gun-cotton has been suspended upon a line in the upper part of my laboratory for about twelve months. It has, therefore, been freely exposed to the air and diffused daylight during that period. A portion of this sample was recently employed in a comparative heat-experiment, with some specially prepared samples, and was found to resist exposure to 100° C. in a very remarkable manner. Several portions have been maintained for many hours at 100°, upon several consecutive days, without undergoing the slightest change, although originally a brief exposure to that temperature sufficed to develope symptoms of decomposition in this gun-cotton.

The behaviour of this specimen led to an examination of several samples of Stowmarket gun-cotton, portions of which had been employed in the heat-experiments described in this memoir, and which have since been exposed to diffused daylight, in loosely stoppered bottles, for about two years and a half. Three among them which, when first examined, were found to undergo decomposition after exposure for a few minutes to 100° C., were selected for re-examination, and they all perfectly resisted decomposition upon long-continued exposure to that temperature.

It thus appears definitely established that the stability of

gun-cotton is importantly increased by long-continued exposure to diffused daylight. An examination into the cause of this interesting fact is now being prosecuted, and the results promise importantly to strengthen the confidence which is already placed in the permanence of gun-cotton.—*June*, 1867.

XLVII.—*Nitrous and Nitric Ethers; their Decompositions and Reactions.*

By E. T. CHAPMAN and M. H. SMITH.

THE following paper contains an account of the effects produced by a considerable number of re-agents upon nitrite of amyl, nitrate of amyl, nitrate of ethyl, and nitrate of methyl. In short, we have attempted to work out in detail a considerable portion of the chemical history of these compounds.

To avoid repetition, we will here state, that whenever in the following pages we speak of a digestion, we mean to imply the heating of the substances together in a flask or retort adapted to an inverted condenser. Any other species of digestion will be specially indicated. We have not thought it necessary to give in full the details of the recognition of the various bodies formed by the decomposition of the substances under examination, as these products were usually of such a kind as to render their identification a matter of great simplicity. A few of the following reactions have been previously described. As they are not always to be found in modern hand-books, we have inserted an account of our own investigations of them, and thus, we trust, have rendered our work more complete.

NITRITE OF AMYL.

The nitrite employed in the following reactions was prepared by saturating amylic alcohol with nitrous acid. The product of this operation was repeatedly washed with water, and dried over ignited carbonate of potash; it was then fractionally distilled, whereby a little apparently unaltered amylic alcohol was separated, together with a very small quantity of a liquid of

lower boiling point. The remainder, which was more than five-sixths of the whole, boiled constantly between 98° and 99°. The nitrous acid employed was obtained by the action of nitric acid on arsenious acid. Though we were a good deal exposed to its vapours, and frequently experienced its strange physiological action, no effects of the slightest permanency were produced.

I. *Nitrite of Amyl and Methylate of Sodium.*—Sodium was dissolved in dry methylic alcohol; and to this solution nitrite of amyl was added, care being taken not to add excess. The reaction was not very vigorous. The mixture was digested for half-an-hour in the water-bath; the products were methyl-amyl-ether, and nitrite of sodium; the reaction, therefore, is strictly analogous to that of iodide of amyl and methylate of sodium:

$$MeNaO + AyNO_2 = MeAyO + NaNO_2.$$

II. *Nitrite of Amyl and Ethylate of Sodium.*—The experiment was performed in a manner precisely similar to that last described, with an analogous result, ethylamyl-ether and nitrite of sodium being the products.

III. *Nitrite of Amyl and Alcoholic Solution of Potash.*—These substances react differently according to the quantity of water present. With much water amylic alcohol was the principal product, with very little water, ethylamyl-ether; frequently a mixture of the two was produced.

IV. *Nitrite of Amyl and Ammonia.*—These substances have little or no action on each other in the cold, or even at the temperature of the water-bath; but if nitrite of amyl be digested in a sealed tube, along with solution of ammonia, at the temperature of 130°, a reaction takes place, nitrogen gas, amylic alcohol, and water being produced, thus—

$$AyNO_2 + NH_3 = AyHO + H_2O + N_2.$$

V. *Nitrite of Amyl and Hydrochloric Acid.*—Concentrated aqueous hydrochloric acid has but little action on the nitrite in the cold; on warming, however, the nitrite becomes coloured, and gas is evolved pretty briskly, but it appears to be difficult to ensure the decomposition of the whole of the nitrite in this manner. This may be readily accomplished by saturating the moist nitrite with hydrochloric acid gas, and digesting the

mixture, still passing the gas into it. Red fumes are evolved during the whole operation. The fluid is at first coloured dark red-brown, but passes through various shades of red, green, and blue, and finally becomes colourless. That portion of the gas which was insoluble in water proved to be pure nitric oxide. The liquid was found to be amylic alcohol, apparently in a state of great purity; it was completely soluble in hydrochloric acid, showing the absence of chloride of amyl. The reaction is as follows :—

$$C_5H_{11}NO_2 + HCl = C_5H_{12}O + NO + Cl.$$

The nitric oxide and chlorine react upon each other in presence of water, forming higher oxides of nitrogen and hydrochloric acid. If care be taken to exclude water from the reaction, a certain amount of chloride of amyl is formed, and at the same time some chlorine substitution-products, but the main portion of the reaction remains unaltered.

VI. *Nitrite of Amyl and Hydrobromic Acid.*—This reaction appears precisely similar to the above, but the products are different. Red fumes are evolved in this case; but though the nitrite be perfectly dry, no free bromine appears. Bromide of amyl is the product, the reaction being as follows :—

$$C_5H_{11}NO_2 + HBr = C_5H_{11}Br + HNO_2.$$

The nitrous acid probably undergoes further decomposition.

VII. *Nitrite of Amyl and Hydriodic Acid.*—This reaction has already been described.* It differs from the two preceding reactions in two particulars. Firstly, no red fume is evolved; secondly, iodine is liberated in considerable quantities. The reaction is as follows :—

$$C_5H_{11}NO_2 + 2HI = C_5H_{11}I + NO + H_2O + I.$$

Ammonia is frequently formed in this reaction.

VIII. *Nitrite of Amyl and Glacial Acetic Acid.*—These substances are completely miscible; they do not react on each other in the cold. On boiling, a slow, continuous action is set up. Nitrite of amyl was digested with excess of glacial acetic acid. During the whole process gas was evolved; during the

* Journal of the Chemical Society [2], iv, 339.

greater part of it red fume, but towards the close pure nitric oxide. The product was acetate of amyl, quite pure, and of perfectly constant boiling point, 140° C. The reaction consists simply in the replacement of nitrous acid by acetic acid:

$$C_5H_{11}NO_2 + C_2H_4O_2 = C_2H_3(C_5H_{11})O_2 + HNO_2.$$

IX. *Nitrite of Amyl and Formic Acid.*—These substances are not miscible; they react very slowly at ordinary temperatures, but rapidly on heating, and the heat generated by the action is so great that not only is all application of external heat unnecessary, but the reaction frequently requires to be checked by the application of cold water. Much gas is evolved, but little or no red fume. The gas is a mixture of carbonic acid and protoxide of nitrogen, together with traces of nitric oxide. The liquid product is formate of amyl. During the whole reaction the liquids in the retort never became more than very slightly coloured; towards its close they became homogeneous, the formate of amyl produced being soluble in the excess of formic acid. The formate obtained was pure, and had a slightly higher boiling-point than that ordinarily assigned to it, viz., 118°. The reaction appears to be as follows:—

$$2C_5H_{11}NO_2 + 4CH_2O_2 = 2CH(C_5H_{11})O_2 + N_2O + 2CO_2 + 3H_2O.$$

X. *Nitrite of Amyl and Chloride of Zinc.*—Strong solution of chloride of zinc acts on the nitrite slowly, even in the cold. On digesting the two substances together, gas is evolved in abundance, and the nitrite gradually dissolves in the solution of chloride of zinc. When the action is complete, the addition of water to the mixture causes an oily layer to rise to the surface. This oil is, however, much coloured. By distilling the whole contents of the flask until no more oil comes over, it may be obtained colourless. It consists of a mixture of valerianic aldehyde and valeranate of amyl. It is a remarkable fact that these two isomeric bodies should be obtained in the same reaction:—

$$2C_5H_{11}NO_2 - H_2O = 2C_5H_{10}O + NO + N, \text{ and}$$

$$2C_5H_{11}NO_2 - H_2O = C_5H_9(C_5H_{11})O_2 + NO + N.$$

XI. *Nitrite of Amyl and Zinc.*—These substances react very

slowly upon each other at the boiling-point of nitrite of amyl. The reaction consists in the expulsion of nitric oxide and the formation of amylate of zinc. The action is extremely slow, and we have not succeeded in pushing it quite to completion. Nitrite of amyl and excess of freshly granulated zinc were digested in the water-bath all day long for six days. During the first five, and a portion of the sixth, nitric oxide was evolved continuously and quite steadily. Towards the end of the sixth day, the evolution of the nitric oxide became even slower than it had been before. The reaction was as follows:—

$$2C_5H_{11}NO_2 + Zn = (C_5H_{11}O)_2Zn + NO.$$

It is worthy of remark, that little or no nitrite of zinc is formed in this reaction. Amylate of zinc appears to have no tendency to decompose the nitrite.

XII. *Nitrite of Amyl and Sodium.*—The reaction between these two bodies is very peculiar, though, at the same time, perfectly simple. When sodium is immersed in nitrite of amyl, it is only very gradually attacked; but the reaction once started, rapidly accelerates, and becomes altogether unmanageable, frequently ending in an explosion. By suitable dilution with ether, however, it may be rendered quite manageable. Gas is evolved in abundance. The gas differs in composition according to circumstances. It is, however, always either nitrogen, protoxide of nitrogen, or a mixture of the two, in varying proportions. When the nitrite, much diluted with ether, is allowed to act on a great excess of sodium, cut into thin pieces, the gas evolved is almost pure nitrogen. If, on the other hand, the sodium is in very small relative quantity, the gas is principally protoxide, especially if the nitrite has not been much diluted with ether. The non-gaseous products, no matter which gas is evolved, are a mixture of amylate of sodium and oxide of sodium. Little or no nitrite of sodium is formed in the reaction. The ether appears to prevent, or, at any rate, greatly to hinder, the decomposition of nitrite of amyl, and also that of the nitrates of amyl, ethyl, and methyl, by the alcoholates of the alkalies. The two reactions which take place may, therefore, be represented as follows:—

(1) $C_5H_{11}NO_2 + 3Na = C_5H_{11}NaO + Na_2O + N.$

(2) $2C_5H_{11}NO_2 + 4Na = 2C_5H_{11}NaO + Na_2O + N_2O.$

Nitrate of Amyl.

We made several attempts to prepare nitrate of amyl in the manner described by Hofmann, viz., distillation of nitric acid, amylic alcohol and urea together. The nitrate is obtainable in this way, but the process is unsatisfactory, the yield being small, and the product contaminated with amylic alcohol; the large quantity of urea required is also an objection. We next attempted to prepare it by the method described by J. Persoz for nitrate of ethyl. A small quantity was prepared in this manner, but most generally the action became unmanageable, and the product was lost. If however the nitric acid be mixed with a sufficient quantity of sulphuric acid, the action becomes much more moderate. We suppose the sulphuric acid to act simply by absorbing any red fume that may be produced, and thus preventing its action. If red fuming nitric acid be mixed with twice its volume of sulphuric acid, the mixture will be found to be perfectly colourless. If the acids used in the preparation of the nitrate (see below) be diluted with water, they evolve red fume, even though themselves colourless. Whatever be the reason, the sulphuric acid does in some way moderate the action. By the following method we have prepared two kilogrammes of nitrate of amyl without the slightest difficulty, and without the evolution of any red fume. One volume of nitric acid of about sp. gr. 1·36 was mixed with two volumes of common concentrated sulphuric acid, and allowed to cool; 150 c.c. of this mixture were placed in a beaker, surrounded by salt and water to which ice had been added, a convenient method of obtaining a constant temperature a degree or two below zero. 50 c.c. of amylic alcohol were now gradually added from a small dropping funnel, the stem of which dipped nearly to the bottom of the mixed acids. During the addition of the alcohol, the liquid was kept constantly stirred, the stem of the dropping funnel itself being used as the stirrer. It took from six to eight minutes to effect the addition of the alcohol. No apparent action took place, except that an oily layer of liquid formed on the surface of the acids. As soon as all the alcohol had been added, the contents of the beaker were transferred to a separating funnel, the acid separated from the nitrate, and the latter run into a flask containing a little water.

By operating in this way 100 parts of amylic alcohol yielded 144 of the nitrate; theoretically they should yield 151. The only point needing particular care in the above process is the stirring; if this be intermitted for more than a few seconds, small white spots, consisting apparently of froth, make their appearance below the surface of the layer of nitrate; if the liquid be not stirred before they have attained any considerable size, a violent action sets in, and the product is lost; with proper stirring however, this accident never occurs. Prepared as above, the nitrate only requires to be washed three or four times, first with dilute solution of potash, and then with warm water, and finally to be dried over chloride of calcium. Thus prepared, nitrate of amyl is a perfectly colourless liquid, boiling quite constantly between 147–8°C. Between 7 and 8°C. its sp. gr. is exactly equal to that of water at the same temperature. Below this temperature it is heavier than water, and above lighter: hence the advantage of using warm water in washing it. The inhalation of its vapour produces headache and a sensation of tightness in the head, accompanied by restlessness. The effects do not pass off for many hours. The nitrate is completely insoluble in water, not even imparting any taste to water with which it is agitated. It is soluble in alcohol, wood-spirit, amylic alcohol, benzol, and glacial acetic acid. It is insoluble in concentrated formic acid, hydrochloric acid, and cold sulphuric and nitric acids. If the nitrate is contaminated with any substance which generates heat on mixture with sulphuric acid, it is completely decomposed by treatment with that acid. Boiling with hydrochloric, acetic, formic, and oxalic acids does not in any way affect it. At its boiling point it dissolves a considerable quantity of sulphur, a portion of which it deposits in crystals on cooling. It dissolves phosphorus pretty freely, but if the solution be boiled for some time, a dull explosion takes place, and the liquid turns black.

Pentachloride of phosphorus is without action upon it in the cold. It may indeed be boiled in this ether, in which case it dissolves and crystallizes unaltered on cooling. On prolonged boiling however, a kind of explosion takes place. Nitrate of amyl may be boiled for hours with terchloride of phosphorus without undergoing alteration. Oxy-chloride on the contrary attacks it vigorously, evolving hydrochloric acid, but no red fumes. Chlorine substitution-products are formed, together with a small

quantity of a basic body. Both the substitution-products and the base have the most unbearable odour. We have not examined them further.

XIII. *Nitrate of Amyl and Methylate of Sodium.* These substances act violently upon each other, but require to be heated before the action will commence; and unless a considerable quantity of the alcohol be present, it takes some time to complete the action by simple digestion. The products are methyl-amyl-ether and nitrate of sodium.

XIV. *Nitrate of Amyl and Alcoholic Solution of Potash.* The action resembles that described in the preceding paragraph, and is likewise greatly facilitated by the presence of alcohol. The products are ethylamyl-ether and nitrate of sodium. With much water, amylic alcohol is produced.

XV. *Nitrate of Amyl and Sodium.* If sodium be added to cold nitrate of amyl, it speedily becomes very bright, and acquires a silvery appearance, gradually changing to golden, and finally the sodium has exactly the colour and appearance of lumps of gold. If the nitrate be kept cool, the reaction stops here, but if it be heated, a violent, but not explosive reaction occurs, no trace of gas is evolved, but the whole becomes a solid mass. On treating this mass with water, nitrite of sodium, amylic alcohol, and caustic soda are obtained. The reaction is as follows:

$$C_5H_{11}NO_3 + 2Na = C_5H_{11}NaO + NaNO_2.$$

On treating the amylate of sodium with water we of course obtain amylic alcohol.

If the nitrate of amyl be diluted with ether, it is at once attacked vigorously by sodium in the cold; and indeed the action of nitrate of amyl, diluted with its own volume of ether, on sodium is exceedingly violent. Without the use of digestion-tubes however, it appears to be impossible to push the action to completion.

Note. About a year ago, Dr. Hugo Müller informed me in conversation, that he had obtained nitrate of amyl by the action of concentrated sulphuric and nitric acids on amylic alcohol.—(Ernest T. Chapman.)

Nitrate of Ethyl.

The nitrate employed was obtained in the ordinary manner by distilling nitric acid, alcohol, and urea together. This ether may be prepared in a manner strictly analogous to that by which we prepared the nitrate of amyl. We did not employ it as a method of preparation, because at the time of making the observation we had already provided ourselves with a sufficient supply of the ether. The process appears to work just as well and just as easily with ethylic alcohol as with amylic alcohol.

Nitrate of ethyl, like nitrate of amyl, is not attacked by formic, acetic, oxalic, or hydrochloric acids; nor in the cold by sulphuric and nitric acids. Trichloride and pentachloride of phosphorus are without action upon it. The oxychloride attacks it, but not very vigorously. The products have not been examined. It is a tolerable solvent for sulphur and phosphorus, but in these respects much inferior to the nitrate of amyl. Heated with alcoholic potash it yields ether, as had previously been obtained by Berthelot.

XVI. *Nitrate of Ethyl and Acetate of Potassium.*—These substances react slowly upon each other when digested in the water-bath; rather more rapidly when alcohol is added to act as a solvent. The products are acetate of ethyl and nitrate of potassium. The reaction is thus perfectly analogous to that which takes place between iodide of ethyl and acetate of potassium.

XVII. *Nitrate of Ethyl and Sodium.*—Cary Lea observed that sodium would keep its metallic lustre for hours when immersed in nitrate of ethyl; it does so, but gradually acquires a golden appearance. With care, the nitrate may even be distilled off the sodium, without any appreciable action. Occasionally, however, a vigorous action is set up, terminating in a violent explosion. The reaction may be rendered manageable by diluting the nitrate with ether, sealing up, and heating in the water-bath. Even under these circumstances the reaction is troublesome in the extreme, either going dangerously fast, or not going at all. When the action is completed and the sodium has disappeared, it will be found that no gas whatsoever has been evolved; on distilling off the ether in the water-bath, and adding water to the residue, and again distilling, alcohol is obtained. The residue in the retort is a mix-

ture of soda and nitrite of sodium. The reaction is therefore strictly analogous to that obtained with nitrate of amyl:

$$C_2H_5NO_3 + 2Na = C_2H_5NaO + NaNO_2.$$

Nitrate of Methyl.

The ordinary method of preparing nitrate of methyl leaves nothing to be desired, nor does there appear to be the smallest danger in operating on a large scale. The reactions of this nitrate closely resemble those of the corresponding ethyl compound.

XVIII. *Nitrate of Methyl and Amylate of Sodium.*—Amylate of sodium was formed by digesting amylic alcohol, diluted with four or five times its volume of ether, with excess of sodium. When the action had terminated, the excess of sodium was removed, and the ether distilled off as far as possible in the water-bath. The amylate of sodium so obtained was digested with the nitrate of methyl. The product was nitrate of sodium and methyl amyl-ether.

XIX. *Nitrate of Methyl and Sodium.*—Nitrate of methyl may be safely distilled from sodium. The sodium rapidly assumes the golden appearance before alluded to, but the reaction stops here. By dilution with ether and digestion in sealed tubes, however, a reaction may be obtained apparently precisely analogous to that which takes place with the nitrate of ethyl. At any rate, nitrite of sodium is formed. The reaction is tiresome in the extreme, far worse than the corresponding nitrate of ethyl reaction.

The foregoing investigation has grown under our hands; originally we intended only to investigate the action of sodium and that of zinc-ethyl on the nitrous and nitric ethers. During the investigation, we were frequently brought to a stand-still, because some point in the natural history of the ethers we were investigating was wanting. Then the main research had to be dropped until the subsidiary question was answered, and during its investigation a similar chain of circumstances would induce us to investigate some other reaction. Hence the desultory and unconnected appearance presented by this paper.

We have but little to offer in the way of comment. The general tendency of the whole investigation is to show the great stability of the nitric ethers, and the extraordinary chemical mobility of the nitrous ethers. We use the words chemical mobility, as the nitrous ethers can scarcely be called unstable, since they exhibit no tendency to spontaneous decomposition.

One of the reactions described in the former part of this paper suggests an inquiry. Ammonia decomposes nitrite of amyl, producing amylic alcohol, water and nitrogen. Supposing we replace the ammonia by ethylamine, should we not in all probability obtain a double ether, viz., ethyl amyl-ether, instead of the alcohol, and would not this probably furnish the most convenient method of recovering the alcohol-radical from compound ammonias?

In conclusion we would point out that although the nitrous ethers differ so remarkably from the nitric ethers in their reactions, yet in many respects they present a very close analogy to them; thus the decompositions of the two classes of ethers by the alcoholates of the alkalis, are strictly analogous; the same is true of the decompositions by nascent hydrogen.

We are now engaged in investigating other reactions of these two classes of ethers.

XLVIII.—*On the Action of Acetic Anhydride upon the Hydrides of Salicyl, Ethyl-salicyl, &c.*

By W. H. Perkin, F.R.S.

Being unable to obtain the hydride of aceto-salicyl (aceto-salicylol) by the process of M. Cahours, viz., by the action of chloride of acetyl upon the hydride of salicyl, I thought it probable that by substituting acetic anhydride for the chloride, a better result might be obtained, the following reaction being expected to take place:—

$$\underset{\text{Hydride of salicyl.}}{\left.\begin{matrix}CO,H\\C_6H_4\\H\end{matrix}\right\}O} + \underset{\text{Acetic anhydride.}}{\left.\begin{matrix}Ac\\Ac\end{matrix}\right\}O} = \underset{\text{Hydride of aceto-salicyl.}}{\left.\begin{matrix}CO,H\\C_6H_4\\Ac\end{matrix}\right\}O} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}Ac\\H\end{matrix}\right\}O.}$$

My anticipation, however, was not realized. A mixture of acetic anhydride and hydride of salicyl, after being heated to 150° C. for four or five hours, remains perfectly fluid, but when agitated with a dilute solution of hydrate of potassium to remove excess of acetic anhydride or hydride of salicyl, it solidifies into a crystalline mass. After pressure between bibulous paper, this new product may be rendered pure by two or three crystallisations from alcohol. When burnt in oxygen it gave the following numbers:—

I. 0·2577 of substance gave
0·5558 of CO_2 and
0·1276 of H_2O.

II. 0·1838 of substance gave
0·3948 of CO_2 and
0·0921 of H_2O.

These numbers gave percentages agreeing with the formula

$$C_{11}H_{12}O_5.$$

as the following comparisons will show:—

	Theory.		Experiment.	
			I.	II.
C_{11}	132	58·93	58·82	58·58
H_{12}	12	5·36	5·50	5·56
O_5	80	35·71	—	—
	224	100·00		

This formula represents a substance composed of acetic anhydride and hydride of salicyl:—

$$C_{11}H_{12}O_5 = C_7H_6O_2, C_4H_6O_3.$$

This body crystallises from alcohol in thick plates with bevelled edges, generally of about 0·2 of an inch in diameter. They are hard and transparent, and fuse at from 103°–104° C. When heated in a retort, this substance distils with partial decomposition. It dissolves rather freely in boiling, but is not easily soluble in cold alcohol. It is insoluble in water.

When heated to 150° C. in a sealed tube with water, it decom-

poses, forming acetic acid and hydride of salicyl, but is not acted upon by cold aqueous hydrate of potassium. Cold nitric acid dissolves it readily, but on the addition of water hydride of salicyl separates as an oil.

Acetic Anhydride and Hydride of Ethyl-salicyl.

These two bodies, when heated in a sealed tube to 150° C. for four or five hours, readily combine. The product is purified by agitation with an aqueous solution of hydrate of potassium, which causes it to solidify into a crystalline mass; it is then pressed between bibulous paper, and twice crystallised from alcohol. A combustion of this product gave the following numbers:—

·2133 of substance gave
·4832 of CO_2 and
·1259 of H_2O.

These numbers give percentages agreeing with the formula

$$C_{13}H_{16}O_5,$$

as the following comparisons will show:—

	Theory.		Experiment.
C_{13}	156	61·90	61·78
H_{16}	16	6·35	6·55
O_5	80	31·75	—
	252	100·00	

This formula, like the preceding, represents a compound of one equivalent of the hydride and one equivalent of the anhydride:—

$$C_{13}H_{16}O_5 = C_9H_{10}O_2, C_4H_6O_3.$$

This body crystallises in small, brilliant, transparent prisms, having bevelled edges. It melts at 88°–89° C., and is easily soluble in hot, but difficultly so in cold, alcohol. It is insoluble in water. Cold aqueous potash is without action upon it, but if heated in a sealed tube with water to 150° C. it decomposes, yielding acetic acid and the hydride of ethyl-salicyl.

Acetic Anhydride and Hydride of Methyl-salicyl.

The hydride of methyl-salicyl combines with acetic anhydride in precisely the same manner as the hydride of ethyl-salicyl. The product may also be purified in the same manner as the preceding.

The resulting compound crystallises in beautiful transparent prisms, melting at 75° C., and more soluble in alcohol than the corresponding ethyl-salicyl derivative. Heated in a sealed tube to 150° C. it decomposes, yielding acetic acid and hydride of methyl-salicyl.

Acetic Anhydride and Hydride of Benzoyl.

Having obtained the foregoing salicyl-derivatives, it appeared to me of importance to study the action of acetic anhydride upon other aldehydes of the aromatic series, and not being aware of the experiments of M. Geuther in this direction, I selected the hydride of benzoyl; but as the process I employed in the preparation of the product previously obtained by this chemist differs in some particulars from his, I have thought it well to describe it here.

Acetic anhydride and hydride of benzoyl are heated together in a sealed tube for several hours to a temperature of 150° C. The product is then transferred to a retort furnished with a thermometer, and heated. After the temperature has risen fifteen or twenty degrees above the boiling point of the hydride of benzoyl, the receiver is changed, and the whole of the remaining product rapidly distilled over. The oily distillate is then agitated with a solution of bisulphite of sodium, to remove any small quantities of hydride of benzoyl that it may contain Crystals then begin to appear, and the oily product rapidly becomes a solid mass of crystals. This crystalline body is purified, first by washing with water, and then by powerful pressure between bibulous paper, until it ceases to produce a greasy stain. A combustion of a specimen prepared in this manner gave the following results :—

·2892 of substance gave
·6709 of CO_2 and
·1541 of H_2O.

These give percentages agreeing with the formula

$$C_{11}H_{12}O_4$$

as the following comparison will show :—

	Theory.		Experiment.
C_{11}	132	63·46	63.26
H_{12}	12	5·77	5·92
O_4	64	30·77	—
	208	100·00	

This substance was first obtained in the crystalline state by Hübner, who found its melting point to be from 44° to 45° C. The product prepared by the above process gave a melting point one degree higher, viz., 45° to 46° C.

This substance is extremely soluble in alcohol and ether, and is remarkable for the magnificent manner in which it crystallises. If only a few grammes be fused in a watch-glass, it will sometimes form on cooling, thick rectangular prisms, an inch in length, and nearly a quarter of an inch in breadth.

Hübner* states that this body is identical with the crystalline diacetate of benzoyl obtained by Limpricht and by Neubauer, by means of acetate of silver and chloride of tolylene $C_7H_6Cl_2$ or dichlorotoluene, and writes its formula—

$$C_7H_6(C_2H_3O_2)_2.$$

From this formula it would appear to be the diacetate of a hydrocarbon radical, and analogous to Wurtz's acetate of ethylene; therefore, reasoning from analogy, it should yield a diatomic alcohol, isomeric with saligenin, if heated with water; but I find that, like the preceding salicyl derivatives, it only decomposes into acetic acid and its aldehyde.

These bodies therefore correspond to the compound of acetic anhydride with ordinary aldehyde, which was discovered by Geuther,† and is only isomeric, and not in any way similar to the acetate of ethylene.

The aldehydic character of a hydride appears to be neutralized by its combination with an anhydride, but what is still

* Bulletin de la Société Chimique de Paris, viii, 93.

† Ann. Ch. Pharm, cvi, 249.

more remarkable, in the case of the hydride of salicyl, the phenolic properties likewise disappear.

I hope to make a further inquiry into the properties of these remarkable compounds. From their decompositions they would appear to be simply direct combinations; but this view appears to be unsatisfactory, especially as the aldehydes form compounds with other bodies of the same type. The following are examples:—

$C_2H_4O.C_2H_3O_2.C_2H_3O$..	Aldehyde	and	acetate of acetyl (acetic anhydride).
$C_2H_4O.Cl.C_2H_3O$	„	„	chloride of acetyl.
$C_2H_4O.CyH$	„	„	cyanide of hydrogen.
$C_7H_6O.C_2H_3O_2.C_2H_3O$	Benzoic aldehyde	and	acetate of acetyl.
$C_7H_6O.Cl.C_7H_5O$	„	„	chloride of benzoyl.
$C_7H_6O.Cy.H$.....	„	„	cyanide of hydrogen.

XLIX.—*Verification of Wanklyn, Chapman, and Smith's Water Analysis on a Series of Artificial Waters.*

By J. Alfred Wanklyn, Professor of Chemistry at the London Institution.

I have thought it desirable to place on record a synthetical proof of the correctness of the new method of determining the organic nitrogenous matters present in waters.

With this object in view, I prepared a dilute solution of albumin, then weighed out small quantities of this solution, and put them into measured quantities of pure water. Having thus prepared a set of waters containing known quantities of impurity, I have submitted them to the new process of analysis, and have compared the analytical results thereby obtained with the synthetical data just mentioned.

The details of this investigation are as follows:—

2·005 grm. of fresh undried white of egg, and 0·910 grm. of dry carbonate of soda were dissolved in water; so much water

was then added until the whole (*i.e.* white of egg, carbonate of soda, and water) weighed 200·5 grm. In this way a one per cent. solution of white of egg was obtained.

This solution was kept in a flask covered in with caoutchouc, and was found to keep unchanged (at least as far as the state of its nitrogen indicated) for a month.

Pure water was obtained by distilling a good natural water which did not contain so much as ·01 milligrm. of free ammonia per litre. The distillation was managed in a glass retort, and was not continued very far so as to avoid decomposing the albuminoïd matter. In this way a distillate was obtained which was remarkably free from ammonia and organic nitrogen. All the experiments about to be described were made with water prepared in this manner. The general way in which I operated was as follows:—

500 c.c. of pure water having been introduced into a retort, a weighed quantity of the one per cent. white of egg solution was next added. Then 8 c.c. of a solution of pure carbonate of soda (containing about 0·5 grm. of carbonate of soda) were added, and the distillation commenced. 100 c.c. of distillate were collected, and then 16 c.c. of potash solution containing 7 to 15 grm. of solid potash was added, and then about 0·5 grm. of permanganate was added, and the distillation proceeded with.

Sometimes 100 c.c. were distilled off between the addition of the potash and the addition of the permanganate.

The 100 c.c. of the first distillate (after the addition of carbonate of soda) were usually almost free from ammonia. ·005, ·007, ·015 milligrm. of NH_3 have been observed in different experiments. A blank experiment with the distilled water gave ·003 milligrm. NH_3

The following table contains the quantity of moist white of egg employed, the "albuminoïd ammonia" (*i.e.* NH_3 evolved by potash and permanganate) found, and the albuminoïd ammonia calculated. The calculation is made on the principle that 1 part of moist white of egg yields 0·0121 parts of NH_3, and is based on experiment.

The moist white of egg left 15 per cent. of dry solid crude albumin when dried at 100° C.

	Moist white of egg milligrammes.	NH_3 found milligramme.	NH_3 (calculated) milligramme.
I.	17·69	0·210	0·214
II.	17·58	0·213	0·2127
III.	41·80	0·505	0·5058
IV.	27·87	0·350	0·337
V.	12·20	0·145	0·1476
VI.	7·47	0·095	0·0904
VII.	23·065	0·275	0·279

In this table the highest number is 41·8 and the lowest 7·47. The range is therefore from 1 to 6. The greatest error is about 5 per cent. on the total quantity of albuminoïd matter employed. The average error is very much smaller. The experiments given in the table are not picked out, but exhibit fairly the degree of accuracy which is attainable. I have given seven examples and have only made nine experiments altogether. This table shows that we can distinguish between $\frac{19}{100}$ and $\frac{20}{100}$ of a milligrm. of albuminoïd ammonia in half a litre of water.

The "albuminoïd ammonia" is not the total amount of ammonia which the albumin is capable of giving, but appears to be $\frac{2}{3}$ of the total quantity, being at any rate a constant fraction of the total quantity.

If, however, instead of adding permanganate of potash along with the caustic potash, or when 200 c.c. of distillate have come over, the boiling with caustic potash be continued to *dryness*, then the total nitrogen or almost the total nitrogen in the albumin may be obtained in the shape of ammonia. This plan, which was adopted in our trial experiment, referred to in the last paper, is inconvenient and not to be recommended in practice, as it converts a very easy process into a difficult one. When we wrote the other paper we did not know that the quantities of ammonia are different in the two processes.

I have also made experiments on the estimation of urea,

0·817 milligrm. urea,
7·470 milligrm. of moist white of egg

were placed in half a litre of water and 8 c.c. of a solution of carbonate of soda containing about 0·5 grm. of carbonate of

soda were added. Distillation was then commenced. There was a very slow evolution of ammonia. Ultimately after long boiling, ·372 milligrm. of ammonia was obtained. Potash and permanganate were then added and ·095 milligrm. of ammonia obtained. Thus we have :—

	Found.	Calculated.
NH_3 from urea	·372	·463
NH_3 albuminoïd	·095	·0904

It will be observed that the estimation of urea is not nearly so sharp as that of albumin. Another experiment gave NH_3 from urea = 1·307 milligrm. Theory required 1·47 milligrm. of NH_3. These determinations of urea are very tedious, and indeed the method is not practicable when the urea is quite pure, and placed in perfectly pure water.

The marked difference in point of stability between perfectly pure urea and urea contaminated with a little albuminoïd matter was recognized long ago, as will be seen on referring to the "Handwörterbuch," article "Harnstoff."

Perfectly pure urea in perfectly pure distilled water may be boiled for a long time with carbonate of soda or with potash without giving off ammonia, as is shown by this experiment :—

1·001 milligrm. of urea was placed in 500 c.c. of distilled water and about 0·5 grm. of carbonate of soda, and about 7 grm. of solid caustic potash added.

				Milligramme NH_3.
(1)	Distillate	100 c.c.	=	·025
(2)	„	100 c.c.	=	·01
(3)	„	100 c.c.	=	.003
(4)	„	80 c.c.	=	·003
(5)	„	50 c.c.	=	·003

The same urea dissolved in a town water containing ·07 milligrm. of albuminoïd ammonia per litre gave a slow evolution of ammonia, becoming after a time quicker.

I need hardly call attention to the fact that the urea occurring in waters contaminated with sewage is not pure urea, and that the circumstance that extreme purity imparts to urea a power

of resistance which impure urea does not possess, does not in the least degree impair the applicability of our method to the case of natural waters.

In conclusion, I have to remark that my results are diametrically opposed to those of Mr. Campbell (see "Laboratory," p. 435) in almost every particular.

Boiling with dilute solution of carbonate of soda does not decompose albumin, even in the dilutest solutions. (Mr. Campbell says the contrary.)

Boiling with caustic potash, and then with permanganate of potash, gives off only about two-thirds of the ammonia which albumin contains (Mr. Campbell got off all the ammonia.)

*The boiling of urea with permanganate of potash along with alkali oxidizes a large proportion of the urea, so as to convert much of its nitrogen into free nitrogen or nitrates. (Mr. Campbell got the whole of the nitrogen of urea converted into ammonia under these circumstances.)

Either the *whole* of the nitrogen of urea must be transformed into ammonia by treatment with alkalies without oxidizing agent, or the transformation cannot be made completely. Impure urea, such as naturally occurs, is easily transformed by alkalis; absolutely pure urea only with difficulty.

* I took ·2355 milligramme of urea equivalent to ·1334 milligramme of NH_3. On distilling with carbonate of soda, potash, and permanganate of potash all added together, I could only get ·039 milligramme of NH_3, *i.e.*, about 30 per cent. In another experiment I got ·575 milligramme of NH_3, instead of 2·675, or about 22 per cent. (*Vide* Wanklyn and Gamgee.)

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 17th, 1867.

Dr. Miller, President, in the Chair.

The following papers were read:—

"On the Amount of Carbonic Acid contained in Sea-air:" by T. E. Thorpe, Dalton Scholar in the Laboratory of Owen's College, Manchester.

"On the Amount of Carbonic Acid contained in the Atmosphere of Tropical Brazil during the Rainy Season:" by T. E. Thorpe.

"Synthetical Researches on Ethers. Part II. Action of Sodium and Isopropylic Iodide upon Ethylic Acetate:" by E. Frankland, F.R.S., and B. F. Duppa, Esq.

"On the Titration of the Compound Ethers:" by Professor Wanklyn.

"On Quantitative Analysis by Limited Oxidation. Examples: Lactic and Diethoxalic Acid:" by Messrs. Ernest T. Chapman and Miles H. Smith.

"On the Preparation of Berberine from *Coscinium Fenestratum*:" by Dr. Stenhouse.

February 7th.

Dr. Miller, President, in the Chair.

James William Hudson, Ph.D., F.S.A., Trafford College, Manchester; Joseph Ince, St. George's Place, Hyde Park

Corner; George Ottley, Doddington Grove, Walworth, were elected Fellows.

The following papers were read:—

"Note on some Varieties of Orchella Weed, and products obtained from them:" by Dr. Stenhouse.

"On the Eggs of *Corixa mercenaria*:" by Dr. T. L. Phipson.

Dr. Matthiessen, F.R.S., delivered a lecture "On Alloys."

February 21st.

Dr. Williamson, Vice-President, in the Chair.

R. R. H. Davy, War Office; H. Weston Eve, Wellington College, Wokingham; Frederick George, Cheltenham; Jonathan Hearder, Plymouth; Martin Henry Payne, Mortimer Street, Cavendish Square; and William Thurston Waite, 37, Jewry Street, were elected Fellows.

The following paper was read:—

"On Limited Oxidation. Determination of the Oxygen Consumed:" by Ernest T. Chapman, Esq.

March 7th.

Dr. Miller, President, in the Chair.

William Price Bonner, Mark Lane; James Campbell Brown, Bonaccord Street, Aberdeen; J. Hersee Freeman, Stratford, Essex; and R. C. Stewart, Prince of Wales' Terrace, Kensington Palace, were elected Fellows.

The following papers were read:—

"On the Oxidation of Formic Acid:" by Ernest T. Chapman, Esq.

"On the Synthesis of Formic and Sulphurous Acids:" by Dr. A. Dupré.

March 21st.

Dr. Miller, President, in the Chair.

Frederick S. Barff, North Audley Street, Grosvenor Square; Angus Frazer, M.D., Union Street, Aberdeen; and Alfred Tribe, Great Portland Street, were elected Fellows.

The following papers were read:—

"On Phospho-nitryl:" by Dr. Gladstone.
"On Phosphide of Magnesium:" by Mr. James Parkinson.

March 30th.

Dr. Miller, President, in the Chair.

Anniversary Meeting (see page 385).

April 4th.

Mr. Warren De la Rue, President, in the Chair.

John Mackay, George Street, Edinburgh; David Skinner Kemp, Bombay, were elected Fellows.

The following papers were read:—

"Note on Mr. Squire's Crystallised Glycerin:" by Dr. Gladstone.
"Experiments on Oxidation by means of Charcoal:" by Professor Crace Calvert.

April 18th.

Dr. Gladstone, Vice-President, in the Chair.

The following papers were read:—

"Observations on the Weathering of Copper Ores:" by Mr. John Spiller.

"On Oxidation of the Acids of the Lactic Series:" by Messrs. Ernest T. Chapman and Miles H. Smith.

"On Limited Oxidation with Alkaline Permanganate:" by Messrs. Ernest T. Chapman and Miles H. Smith.

"On the Presence of Soluble Phosphates in Cotton Fibre, Seeds, &c.: by Professor Crace Calvert.

May 2nd.

Dr. Miller, Vice-President, in the Chair.

John Cargill Brough, Norman Terrace, Stockwell; and F. W. Peterson, Myddleton Square; were elected Fellows.

Dr. Odling made a verbal communication "On Combination by the alleged Saturation of Atomicities."

May 18th.

Mr. Abel, Vice-President, in the Chair.

The following papers were read:—

"On Coumarin:" by Mr. W. H. Perkin.

"On the Constitution of Phosphites:" by Prof. Rammelsberg.

"On the Changes in the Proportion of Acid and Sugar present in Grapes, during the Process of Ripening:" by Dr. A. Dupré.

"On some of the Changes produced by the addition of Plaster of Paris to Must:" by Dr. A. Dupré.

"On an apparatus for preventing the escape of Sulphuretted Hydrogen:" by the Rev. B. W. Gibsone, M.A., B. Sc.

"On the Practical Loss of Soda in the Alkali Manufacture:" by C. R. A. Wright, B. Sc.

June 6th.

Dr. Williamson, Vice-President, in the Chair.

Sir Benjamin Brodie delivered a lecture, "On Ideal Chemistry."

June 20th.

Mr. Warren De la Rue, President, in the Chair.

The following papers were read:—

"On some New Derivatives of the Hydrides of Salicyl:" by Mr. W. H. Perkin.

"On Pyrophosphoric Acid:" by Dr. Gladstone.

"On Water Analysis—Determination of the Nitrogenous Organic Matter:" by Messrs. J. A. Wanklyn; E. T. Chapman; and M. H. Smith,

"Analysis of a Biliary Concretion, and on a New Method of preparing Biliverdin:" by Dr. T. L. Phipson.

"On the Action of Chloride of Iodine upon Picric Acid:" by Dr. Stenhouse.

"On Julin's Chloride of Carbon:" by Mr. Bassett.

Donations to the Library in the year 1867:—

"A Dictionary of Chemistry and the Allied Branches of other Sciences:" by Henry Watts. Parts xxxvii—xlii: from Messrs. Longman and Co.

"Chemistry Inorganic and Organic, with Experiments, and a Comparison of Equivalent and Molecular Formulæ:" by C. L. Bloxam: from the Author.

"Outline Facts of Chemistry, with Exercises:" by T. Ward: from the Author.

"Inventors and Inventions:" by Henry Dircks: from the Author.

"Miscellanies; being a Collection of Essays on Literary Subjects, published at various times:" by C. G. Daubeny: from the Author.

"The Chemical Laboratories of the Universities of Bonn and Berlin:" by A. W. Hofmann: from the Science and Art Department of the Committee of Council on Education.

"The Calculus of Chemical Operations. Part I; on the Construction of Chemical Symbols:" by Sir B. C. Brodie, Bart.: from the Author.

"Abridgements of Specifications relating to Photography:" Compiled by W. H. Walenn: from the Compiler.

"Abridgements of Specifications relating to the Plating and Coating of Metals by Metals:" Compiled by W. H. Walenn: from the Compiler.

"A Course of Lectures on Coal-gas:" delivered at the Royal Institution of Great Britain: by E. Frankland: from the Author.

"On Vital Force; its Pulmonic Origin and the General Laws of its Metamorphosis:" by T. G. Hake: from the Author.

"A new Chemical Nomenclature:" by S. D. Tillman, of New York: from the Author.

"Researches on Acids of the Lactic Series:" Part I, "Synthesis of Acids of the Lactic Series:" by E. Frankland and B. F. Duppa: from the Authors.

"On some Fluorine-Salts of Antimony:" by C. Marignae: from the Author.

"On Amido-valerianic Acid:" by John Clark: from the Author.

"Researches on Solar Physics;" 2nd Series. Area measurements of the Sun-spots observed by Carrington during the seven years from 1854 to 1860 inclusive, and deductions therefrom: by Warren De la Rue, Balfour Stewart, and Benjamin Loewy: from Warren De la Rue, Esq.

"On the Construction of a Normal Map of the Solar Spectrum:" by Wolcott Gibbs: from the Author.

"On some Effects of a Fluid in Motion:" by G. F. Rodwell: from the Author.

"Field Experiments with Clover Seeds:" by Dr. Völcker.

"On Disinfectants:" by Dr. Völcker: from the Author.

"Experimental Investigations connected with the supply of Water from the Hooghly to Calcutta: by David Waldie: from the Author.

"Third Report of the Commissioners appointed to inquire into the best means of Preventing the Pollution of Rivers (Rivers Aire and Calder):" Vol. I, Reports, Appendix, Plans.—Vol. II, Minutes of Evidence and Index: from the Commissioners.

"Report of the Committee of the British Association on Unformity of Weights and Measures (1866):" from the Committee.

"Report on Epidemic Cholera in the Army of the United States during the year 1866:" from the Surgeon-General.

"The International Horticultural Exhibition and Botanical Congress, held in London, May, 1866; Report of Proceedings:" from the Committee.

"Christianity and Rationalism in their Relations to Natural Science:" by C. G. Daubeny: from the Author.

"Theology and Natural Science, their mutual relations; a Lecture by J. H. Gladstone:" from the Author.

"The Polytechnic College, a proposed Institution for aiding depressed talent to complete works in progress connected with Science, Literature, and Art:" from the Author.

"Les Parfums et les Cosmétiques; par S. Piesse; traduit par G. Reveil:" from S. Piesse, Esq.

"Dénaturation et Utilisation des Résidus des Fabriques de Soude et de Chlore; Régénération du Soufre:" from the Société Anonyme des Anciennes Salines domaniales de l'Est.

"Sintesi degli Alcoli per mezzo dell' Etere clorurato:" per A. Lieben.

"Sulla Costituzione dei Carburi d'Idrogeno;" per A. Lieben: from the Author.

"Studi sul Corpo luteo della Vacca:" per G. Piccolo e A. Lieben: from the Authors.

"Libros del Saber de Astronomia, del Rey Don Alfonso de Castilla," compilados, anotados y comentados: por Don Manuel Rico y Sinobras:
from the Royal Academy of Sciences at Madrid.

"Die Bedeutung moderner Gradmessungen;" by Dr. C. M. Bauernfeind:
from the Royal Bavarian Academy of Sciences.

"Die Entwickelung der Ideen in der Naturwissenschaft:" von Justus v. Liebig:
from the Royal Bavarian Academy of Sciences.

"Ueber die Brauchbarkeit der in verschiedenen europäischen Staaten veröffentlichten Resultate des Recrutirungs-Geschäftes zur Beurtheilung des Entwickelungs- und Gesundheits-Zustandes ihrer Bevölkerungen:" von Dr. T. L. W. Bischoff, 8vo., München, 1867.

Periodicals :—

"Philosophical Transactions," 1866, parts I, II, and III; 1867, part I: from the Royal Society.

"List of Officers and Fellows of the Royal Society for the year 1866:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh," vol. xxiv, part II; for the session 1865–66.

"Proceedings of the same;" session 1865–66: from the Society.

"Memoirs of the Royal Astronomical Society," vol. XXXV.

"Monthly Notices of the same, 1867:" from the Society.

"Quarterly Journal of the Geological Society," for 1867: from the Society.

"Quarterly Journal of Science," for 1866: from the Editor.

"Proceedings of the Royal Institution of Great Britain," vol. V.

"List of Members, Officers, and Professors of the same," for 1867: from the Royal Institution.

"Journal of the Photographic Society," for 1867: from the Society.

"Pharmaceutical Journal and Transactions," for 1867: from the Editor.

"Calendar of the Pharmaceutical Society," 1857: from the Society.

"Journal of the Society of Arts," 1867: from the Society.

"Chemical News," 1867: from the Editor.

"The Laboratory, a Weekly Record of Scientific Research:" from the Editor.

"Thirty-fourth Annual Report of the Royal Cornwall Polytechnic Society," 1866: from the Society.

"Annual Report of the Leeds Philosophical and Literary Society," 1865–66: from the Society.

"American Journal of Science and Art," from November, 1866, to September, 1867: from the Editor.

"Journal of the Franklin Institute," from November, 1866, to October, 1867: from the Institute.

"Annual Report of the American Institute of the City of New York," 1866: from the Institute.

"Annual Report of the Board of Regents of the Smithsonian Institution, 1866.

"Smithsonian Miscellaneous Collections," vol. VI.: from the Smithsonian Institution.

"Annual Report of the Secretary at War (U.S.), with accompanying papers:" from E. M. Stanton, Secretary at War.

"Transactions of the Albany Institute," vol. V.: from the Institute.

"Transactions of the Connecticut Academy of Sciences," vol. I, part 1: from the Academy.

"Cosmos," 2me série—Tome IV: from the Editor.

"Bulletin de l'Académie des Sciences de St. Pétersbourg:" Tomes X, XI: from the Academy.

"Bulletin de l'Académie Royale de Belgique," 1867.

"Annuaire de l'Académie Royale de Belgique," 1867: from the Academy.

"Giornale di Scienze naturali ed economiche, publicati per cura del Consiglio di Perfezzionamente annesso all R. Istituto technico di Palermo," volume II, fascicoli 2, 3, 4: from the Institute.

"Abhandlungen der königlich-baierischen Akademie der Wissenschaften in München," Band X, Abtheilung I.

"Sitzungsberichte derselben," 1867, Band I, Hefte 1—4; Band II, Heft 1: from the Royal Bavarian Academy of Sciences.

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften in Wien (mathematisch-physikalische Classe)," 1866, Abth. I, Hefte 7, 8; Abth. II, Hefte 6—9: from the Imperial Academy of Sciences at Vienna.

"Zeitschrift für Chemie. Neue Folge; herausgegeben von A. Hübner," Band III, Hefte 18—24; Band IV, Hefte 1—9.

"Verhandlungen der naturforschenden Gesellschaft in Basel," Abth. IV, Heft 3: from the Society.

"Vierteljahrsschrift der naturforschenden Gesellschaft in Zürich," 1864, 1865, 1866: from the Society.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs Forhandlinger, og des Medlemmers Arbeeten," 1867: from the Royal Danish Academy of Sciences.

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